

Some of the most important chemical reactions for sustaining life, for energy production and storage, and for maintaining the delicate biogeochemical balance of our oceans and atmosphere are classified as redox reactions.

In this chapter you will learn how redox reactions can be defined in terms of electron transfer, and how this definition can be extended by using the concept of oxidation number. You will construct balanced half-equations that describe the transfer of electrons, and then combine these half-equations to create an overall equation for the reaction. You will also learn about the practical implications of redox reactions involving metals, including consideration of: the reactivity series of metals; metal displacement reactions; and the corrosion of metals—including ways to prevent corrosion.

## Syllabus subject matter

### Topic 2 • Oxidation and reduction

#### ■ REDOX REACTIONS

- recognise that a range of reactions, including displacement reactions of metals, combustion, corrosion and electrochemical processes, can be modelled as redox reactions involving oxidation of one substance and reduction of another substance
- understand that the ability of an atom to gain or lose electrons can be predicted from the atom's position in the periodic table, and explained with reference to valence electrons, consideration of energy and the overall stability of the atom
- identify the species oxidised and reduced, and the oxidising agent and reducing agent, in redox reactions
- understand that oxidation can be modelled as the loss of electrons from a chemical species, and reduction can be modelled as the gain of electrons by a chemical species; these processes can be represented using balanced half-equations and redox equations (acidic conditions only)
- deduce the oxidation state of an atom in an ion or compound and name transitional metal compounds from a given formula by applying oxidation numbers represented as Roman numerals
- use appropriate representations, including half-equations and oxidation numbers, to communicate conceptual understanding, solve problems and make predictions.

#### ■ MANDATORY PRACTICAL 2

- Perform single displacement reactions in aqueous solutions.



## 5.1 Introducing redox reactions



### BY THE END OF THIS MODULE YOU SHOULD BE ABLE TO:

- describe redox reactions in terms of electron transfer
- recall that oxidation involves loss of electrons and reduction involves gain of electrons
- represent simple redox reactions using half-equations
- identify oxidising and reducing agents for simple redox reactions
- understand the reactivity of metals and metal displacement reactions in terms of redox processes
- understand the causes and effects of corrosion in terms of redox processes.

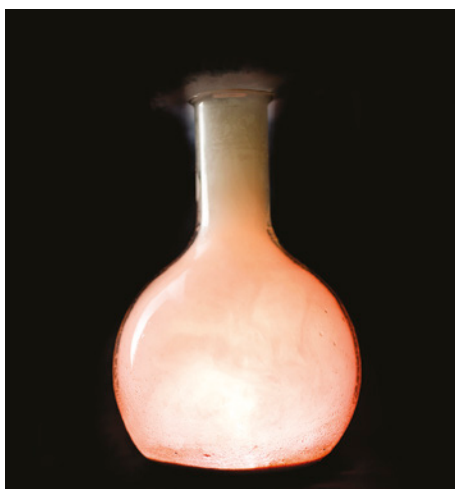


FIGURE 5.1.1 Potassium burning in chlorine gas—a spectacular example of a redox reaction

Your everyday life depends on a large number of chemical reactions. Many of these are **redox reactions**. The term 'redox' is derived from the specific reduction and oxidation processes that, when combined, complete the overall redox reaction.

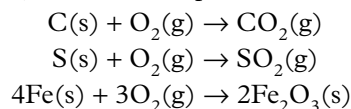
Redox reactions are occurring within you and around you all the time. From the respiration reactions that enable your cells to produce energy, and the combustion reactions that warm your home, to the reactions in the batteries that keep your mobile phone working. The spectacular reaction between potassium and chlorine gas shown in Figure 5.1.1 is also an example of a redox reaction.

### REDOX REACTIONS—ELECTRON TRANSFER REACTIONS

Fundamentally, redox reactions involve a transfer of electrons from one chemical species to another. The atom, molecule or ion that loses electrons in a redox process is said to have undergone **oxidation**—oxidation involves loss of electrons. The atom, molecule or ion that gains electrons during a redox reaction is said to have undergone **reduction**—reduction involves a gain of electrons.

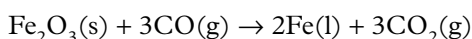
### Early understandings of redox reactions

When chemistry evolved from the ancient study of alchemy, many of the reactions known to early chemists involved air. French chemist Antoine Lavoisier identified the reactive component of air and named it oxygen. As a result, reactions in which oxygen was a reactant were described as oxidation reactions. In air, the combustion of an element such as carbon, sulfur or iron produces an oxide:



Because elemental iron reacts readily with oxygen, iron is generally found in nature in ores containing minerals, such as haematite ( $\text{Fe}_2\text{O}_3$ ) and magnetite ( $\text{Fe}_3\text{O}_4$ ). The iron metal used extensively for construction has been extracted from iron ore in a blast furnace.

The extraction of iron from iron ore in a blast furnace can be represented by the equation:



In this reaction, the iron(III) oxide has lost oxygen and the carbon monoxide has gained oxygen. The iron(III) oxide is described as having been **reduced** and the carbon monoxide is described as having been **oxidised**.

### Origins of the words 'oxidation' and 'reduction'

Scientists first used the term 'oxidation' in the late 18th century after the work of Antoine Lavoisier. Lavoisier showed that the 'burning' of metals, such as mercury, involved a combination with oxygen.

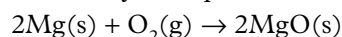
The term ‘reduction’ was used long before this to describe the process of extracting metals from their ores. The word ‘reduction’ comes from the Latin *reduco*, meaning to restore.

The process of metal extraction was seen as restoring the metal from its compounds, such as iron from iron oxide or copper from copper(II) oxide. The reduction of copper(II) oxide to form copper powder occurs when copper(II) oxide is heated in the presence of hydrogen or methane gas, as shown in Figure 5.1.2. Some fine particles of copper escape with the gas, causing the green flame.

## Transfer of electrons

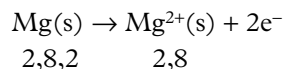
Figure 5.1.3 shows that when a piece of magnesium ribbon is heated in a flame it burns with a brilliant white flame. Magnesium oxide powder is the product formed from this chemical reaction.

This reaction can be represented by the equation:



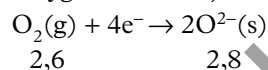
The reaction involves a loss and gain of electrons by the reactants, which can be represented by two **half-equations**.

Each magnesium atom loses two electrons to form a magnesium ( $\text{Mg}^{2+}$ ) ion. The half-equation for this part of the overall reaction is written as shown. The electronic configurations are also shown:



Notice that when electrons are lost, they appear as products (on the right-hand side) in the half-equation.

At the same time, each oxygen atom in the oxygen molecule ( $\text{O}_2$ ) gains two electrons (i.e. four electrons per oxygen molecule):



Notice that when electrons are gained, they appear as reactants (on the left-hand side) in the half-equation. The electrons that are gained by the oxygen have come from the magnesium atoms.

Note that there is no overall loss of electrons, but a transfer of electrons from one atom to another. If an atom, ion or molecule loses electrons, there must be another atom, ion or molecule that gains electrons. Therefore, oxidation and reduction always occur simultaneously and cannot occur independently of one another.

Atoms also lose and gain electrons in many other reactions, and this transfer of electrons provides a widely used definition of oxidation and reduction.

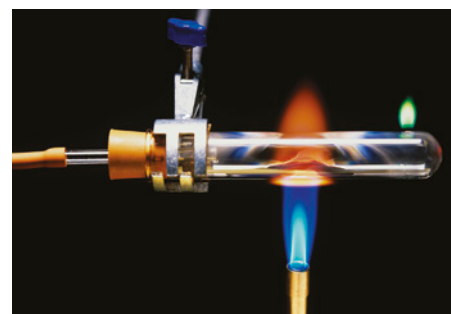
The simple mnemonic ‘OIL RIG’ can be used to assist in remembering the differences between oxidation and reduction processes:

**O**xidation  
**I**s  
**L**oss

**R**eduction  
**I**s  
**G**ain

### Electron transfer, electron configurations and the periodic table

The burning of magnesium described above involves metal magnesium atoms losing electrons and non-metallic oxygen atoms gaining electrons. You may recall from Units 1 and 2 that metals have relatively low electronegativity values and relatively low ionisation energies. This means that metal atoms have a relatively low tendency to draw valence electrons to themselves within chemical bonds and tend to lose valence electrons to other species in chemical reactions. In other words, metals tend to undergo oxidation during chemical reactions. Conversely, non-metals have relatively high electronegativity values and high electron affinity values. This means that non-metals



**FIGURE 5.1.2** The reduction of copper(II) oxide to form copper powder occurs when it is heated in the presence of hydrogen or methane gas.



**FIGURE 5.1.3** Magnesium ribbon burns brightly when heated in air to form a white powder, magnesium oxide.

**i** Oxidation is defined as the loss of electrons.  
Reduction is defined as the gain of electrons.



have a strong tendency to draw valence electrons to themselves in chemical bonds and tend to gain electrons from other species in chemical reactions. In other words, non-metals tend to undergo reduction during chemical reactions.

When a metal atom loses electrons, the atom becomes a stable cation with a stable electron configuration. In the case of the magnesium atom there are 12 electrons in total, with two electrons in the valence shell. The full electron configuration is 2,8,2. The loss of the two valence electrons leads to the formation of the  $Mg^{2+}$  ion, which has an electron configuration equivalent to that of the noble gas, neon (i.e. 2,8)—which we know is a very stable electron configuration.

When a non-metal atom gains electrons, the atom becomes a stable anion with a stable electron configuration. In the case of the oxygen atom, there are eight electrons in total with six electrons in the valence shell. The full electron configuration of oxygen is 2,6 and the valence shell can readily accommodate (or accept) two more electrons. The gain of two valence electrons forms the  $O^{2-}$  ion which also has the stable electron configuration of neon (i.e. 2,8).

When atoms undergo redox processes the number of electrons transferred is determined by the electron configurations of the atoms involved. Electrons are lost or gained to achieve a stable electron configuration. For main group elements this means that the position of the element in the periodic table can be used to predict how many electrons will be lost or gained.

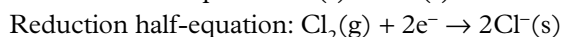
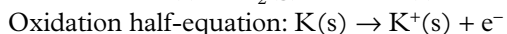
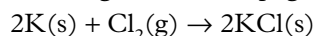
Figure 5.1.4 shows the stable ions for a range of main group elements. We can see that **main group metals** lose enough electrons to achieve the same number and arrangement of electrons as the noble gas immediately preceding it in the periodic table. Conversely, main group non-metal elements will gain enough electrons to achieve the same number and arrangement of electrons as the noble gas immediately following it in the periodic table.

|  |        |           |   |   |   |   |   |   |   |    |    |    |           |    |    |          |           |        |             |
|--|--------|-----------|---|---|---|---|---|---|---|----|----|----|-----------|----|----|----------|-----------|--------|-------------|
|  | 1      |           |   |   |   |   |   |   |   |    |    |    |           |    |    |          |           |        | 18          |
|  |        | 2         |   |   |   |   |   |   |   |    |    |    |           | 13 | 14 | 15       | 16        | 17     | Noble gases |
|  | $Li^+$ |           |   |   |   |   |   |   |   |    |    |    |           |    |    | $N^{3-}$ | $O^{2-}$  | $F^-$  |             |
|  | $Na^+$ | $Mg^{2+}$ | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | $Al^{3+}$ |    |    |          | $S^{2-}$  | $Cl^-$ |             |
|  | $K^+$  | $Ca^{2+}$ |   |   |   |   |   |   |   |    |    |    | $Ga^{3+}$ |    |    |          | $Se^{2-}$ | $Br^-$ |             |
|  | $Rb^+$ | $Sr^{2+}$ |   |   |   |   |   |   |   |    |    |    |           |    |    |          | $Te^{2-}$ | $I^-$  |             |
|  | $Cs^+$ | $Ba^{2+}$ |   |   |   |   |   |   |   |    |    |    |           |    |    |          |           |        |             |

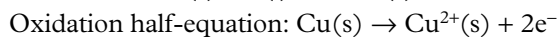
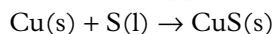
FIGURE 5.1.4 Predicting ionic charges using the periodic table

### Other examples of redox reactions

Many redox reactions do not involve a reaction with oxygen. The reaction between potassium and chlorine shown in Figure 5.1.1 on page 118 is an example:



Another example is the reaction between copper and liquid sulfur:



You will note that in each of the above chemical equations the charge on each of the atoms changes during the chemical reaction. A change in electrical charge on atoms, ions or molecules is one way that chemical reactions can be identified as redox reactions.

## Worked example 5.1.1

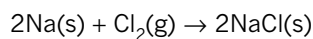
### UNDERSTANDING SIMPLE OXIDATION AND REDUCTION REACTIONS

|   |  |
|---|--|
| Construct the oxidation and reduction half-equations for the reaction with the overall equation:<br>$2\text{Li(s)} + \text{Br}_2\text{(l)} \rightarrow 2\text{LiBr(s)}$ |  |
| <b>Thinking</b>   | <b>Working</b>   |
| Identify the ions in the product.   | LiBr is made up of $\text{Li}^+$ and $\text{Br}^-$ ions.                 |
| Construct the half-equation for the oxidation of the reactant that forms positive ions and balance the equation with electrons.   | $\text{Li(s)} \rightarrow \text{Li}^+\text{(s)} + \text{e}^-$            |
| Construct the half-equation for the reduction of the reactant that forms negative ions and balance the equation with electrons.   | $\text{Br}_2\text{(l)} + 2\text{e}^- \rightarrow 2\text{Br}^-\text{(s)}$ |

### ► Try yourself 5.1.1

### UNDERSTANDING SIMPLE OXIDATION AND REDUCTION REACTIONS

Construct the oxidation and reduction half-equations for the reaction with the overall equation:

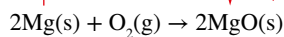
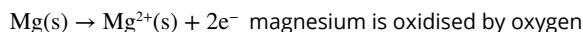


## Oxidising agents and reducing agents

Just as an employment agent enables a client to become employed, an **oxidising agent** or **oxidant** enables or causes another chemical to be oxidised. Similarly, a **reducing agent**, or **reductant**, enables or causes another chemical to be reduced. Redox reactions always involve an oxidising agent and a reducing agent that react together.

In the reaction between magnesium and oxygen shown in Figure 5.1.5, magnesium is being oxidised by oxygen. So, oxygen is the oxidising agent. In turn, oxygen is gaining electrons from magnesium. It is being reduced by the magnesium, so magnesium is the reducing agent.

Reaction with  $\text{O}_2$  causes Mg to lose electrons.  
 $\text{O}_2$  is the oxidising agent.



Reaction with Mg causes  $\text{O}_2$  to gain electrons.  
Mg is the reducing agent.



**FIGURE 5.1.5** In the reaction between magnesium and oxygen, magnesium is the reducing agent and oxygen is the oxidising agent.

Since metals tend to lose electrons, they act as reducing agents. Conversely, since non-metals tend to gain electrons, they act as oxidising agents.

Figure 5.1.6 on page 122 summarises the list of redox terms introduced in this module.

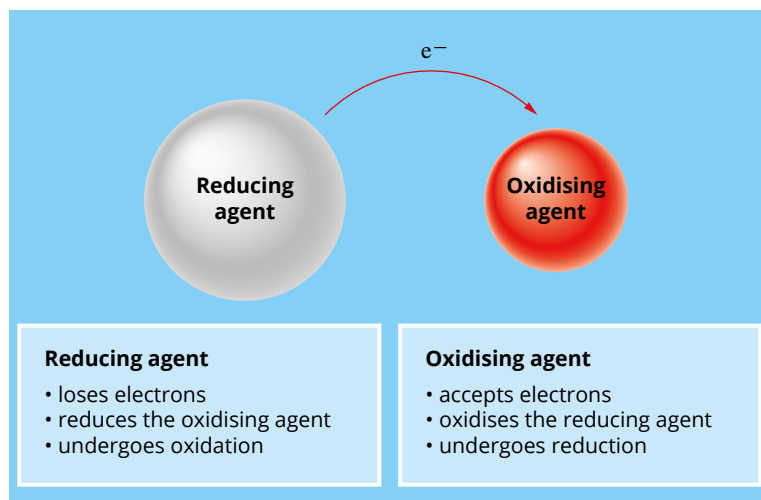


FIGURE 5.1.6 Summary of redox reaction terms

**i** Reducing agents cause another chemical to be reduced. In the reaction, they are oxidised.  
Oxidising agents cause another chemical to be oxidised. In the reaction, they are reduced.

## Balancing simple redox equations

Half-equations enable you to see the detail of what is happening in a redox reaction. Like other chemical equations, half-equations must be balanced so there is the same number of atoms of each element on each side of the arrow. Similarly, charge must also be balanced. Half-equations and full redox equations should indicate the states of all the species in the reaction as well.

### Worked example 5.1.2

#### WRITING SIMPLE HALF-EQUATIONS

When sodium metal reacts with fluorine gas ( $F_2$ ), solid sodium fluoride is formed. The oxidation and reduction reactions can be represented by two half-equations.

Construct these half-equations and identify the substances that are oxidised and reduced.

| Thinking  | Working   |
|---|---|
| Identify one reactant and the product it forms and represent them on each side of an equation.<br>Balance the equation for the element.         | $F_2(g) \rightarrow 2F^-(s)$  |
| Add electrons to balance the equation for charge.   | $F_2(g) + 2e^- \rightarrow 2F^-(s)$   |
| To decide whether the reactant is oxidised or reduced, remember that oxidation is loss of electrons and reduction is gain of electrons.         | Electrons are gained, so this is reduction.<br>The $F_2(g)$ is being reduced. |
| Identify the second reactant and the product it forms, and represent them on each side of an equation.<br>Balance the equation for the element. | $Na(s) \rightarrow Na^+(s)$   |
| Add electrons to balance the equation for charge.   | $Na(s) \rightarrow Na^+(s) + e^-$   |
| To decide whether the reactant is oxidised or reduced, remember that oxidation is loss of electrons and reduction is gain of electrons.         | Electrons are lost, so this is oxidation.<br>The $Na(s)$ is being oxidised.   |

### ► Try yourself 5.1.2

#### WRITING SIMPLE HALF-EQUATIONS

When a piece of copper metal is placed into a silver nitrate solution, silver metal is formed and the solution gradually turns blue, indicating the presence of copper(II) ions in the solution. The oxidation and reduction reactions can be represented by two half-equations.

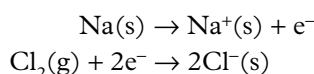
Construct these half-equations and identify the substances that are oxidised and reduced.

### Writing an overall redox equation

When writing equations for redox reactions, the two half-equations are normally written first and then added together to obtain an overall equation.

An overall equation does not show any electrons transferred; all the electrons lost in the oxidation reaction are gained in the reduction reaction. One, or perhaps both, of the half-equations may need to be multiplied by a factor to ensure that the electrons balance and can be cancelled out in the overall equation.

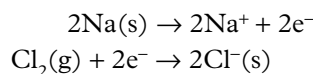
Consider the reaction of sodium and chlorine gas. In this reaction, each Na atom is oxidised and loses one electron. Each Cl<sub>2</sub> molecule is reduced and gains two electrons:



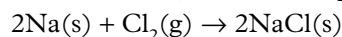
Two Na atoms must therefore be oxidised to provide the electrons required by each chlorine molecule that is reduced. To write an overall equation for this reaction, the half-equation involving the oxidation of Na is multiplied by a factor of two before combining it with the half-equation for reduction of Cl<sub>2</sub>:



You can now write the two half-equations and add them to find the overall equation:



When the electrons have been cancelled, the overall equation is:

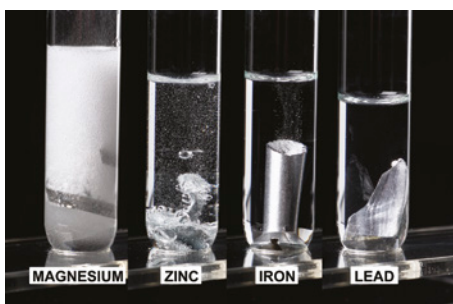


**i** When writing an overall redox equation from two half-equations, you need to balance the number of electrons.

### Worked example 5.1.3

#### BALANCING OVERALL REDOX EQUATIONS FROM HALF-EQUATIONS

|  |   |
|--|---|
| Sodium metal is oxidised by oxygen gas in air to form solid sodium oxide.<br>Construct the half-equations for the reaction and hence construct the balanced overall equation.  |   |
| <b>Thinking</b>  | <b>Working</b>  |
| Identify one reactant and the product it forms, and represent them on each side of the equation.<br>Balance the equation for the element.  | $\text{O}_2(\text{g}) \rightarrow 2\text{O}^{2-}(\text{s})$   |
| Add electrons to balance the equation for charge.  | $\text{O}_2(\text{g}) + 4\text{e}^- \rightarrow 2\text{O}^{2-}(\text{s})$   |
| Identify the second reactant and the product it forms, and represent them on each side of the equation.<br>Balance the equation for the element.   | $\text{Na(s)} \rightarrow \text{Na}^+(\text{s})$  |
| Add electrons to balance the equation for charge.  | $\text{Na(s)} \rightarrow \text{Na}^+(\text{s}) + \text{e}^-$   |
| Multiply one equation by a suitable factor to ensure that the number of electrons is balanced. In this case we multiply the oxidation half-equation by four since the reduction of oxygen requires four electrons so the oxidation of sodium must supply four electrons. | $(\text{Na(s)} \rightarrow \text{Na}^+(\text{s}) + \text{e}^-) \times 4$<br>$4\text{Na(s)} \rightarrow 4\text{Na}^+(\text{s}) + 4\text{e}^-$  |
| Add the oxidation and the reduction half-equations together, cancelling out electrons so that none are in the final equation. Combine ions to create the formula of the product.   | $\text{O}_2(\text{g}) + 4\text{e}^- \rightarrow 2\text{O}^{2-}(\text{s})$<br>$4\text{Na(s)} \rightarrow 4\text{Na}^+(\text{s}) + 4\text{e}^-$<br>When the electrons have been cancelled, the overall equation is:<br>$4\text{Na(s)} + \text{O}_2(\text{g}) \rightarrow 2\text{Na}_2\text{O(s)}$ |



**FIGURE 5.1.7** Some metals react with dilute acid to form a salt and hydrogen gas. The reaction between magnesium and dilute acid is extremely vigorous. The reaction between zinc and dilute acid is less vigorous. The reaction between iron and dilute acid is very slow. There is no reaction between lead and dilute acid. Based on this information, the order of metal reactivity from most reactive to least reactive is magnesium, zinc, iron and lead.

### ► Try yourself 5.1.3

#### BALANCING OVERALL REDOX EQUATIONS FROM HALF-EQUATIONS

Aluminium metal is oxidised by oxygen gas in air to form solid aluminium oxide. Construct the half-equations for the reaction and hence construct the balanced overall equation.

#### THE REACTIVITY SERIES OF METALS

When metals undergo corrosion, some react quickly and vigorously with oxygen and water, and even more vigorously with acids. The reaction between other metals with oxygen is quite slow. Copper pipes oxidise slowly in the air, producing a brown-black copper oxide coating, while the reaction of magnesium ribbon in acid is more vigorous. These are both examples of redox reactions.

This module will examine the reactivity of different metals and describe how to write equations for reactions between metals and solutions of metal ions.

#### Reactivity of metals

Sodium, magnesium and iron are metals that are relatively easily oxidised. Sodium is oxidised so readily that it has to be stored under paraffin oil to prevent it from reacting with oxygen in the atmosphere. The oxidation of iron, which can eventually result in the formation of rust, can be an expensive problem.

Other metals do not corrode as readily. For example, platinum and gold are sufficiently inert and are found as pure elements in nature.

Figure 5.1.7 shows a comparison of four different metals reacting with dilute acid. By observing how readily metals react with oxygen, water, dilute acids and other metal salts, it is possible to determine an order of reactivity of metals.

The metals can be ranked in a list according to their reactivity, or ability to act as reducing agents. Figure 5.1.8 shows such a ranking, which is also known as a **reactivity series of metals**. Figure 5.1.9 shows the reduction half-equations for the metal cations as each cation gains electrons to form the corresponding metal.

| Element          | Reactivity        |
|------------------|-------------------|
| K                | most reactive<br> |
| Na               |                   |
| Li               |                   |
| Ba               |                   |
| Sr               |                   |
| Ca               |                   |
| Mg               |                   |
| Al               |                   |
| C*               |                   |
| Mn               |                   |
| Zn               |                   |
| Cr               |                   |
| Fe               |                   |
| Cd               |                   |
| Co               |                   |
| Ni               |                   |
| Sn               |                   |
| Pb               |                   |
| H <sub>2</sub> * |                   |
| Sb               |                   |
| Bi               |                   |
| Cu               |                   |
| Hg               |                   |
| Ag               |                   |
| Au               |                   |
| Pt               |                   |
|                  | least reactive    |

\* Carbon (C) and hydrogen gas (H<sub>2</sub>) added for comparison

**FIGURE 5.1.8** Reactivity series of metals

|   |  |
|---|--|
| weakest oxidising agent<br>increasing oxidising agent strength<br>strongest oxidising agent | strongest reducing agent<br>increasing reducing agent strength<br>weakest reducing agent |
|---|--|

$\text{Li}^+(\text{aq}) + \text{e}^- \rightarrow \text{Li}(\text{s})$   
 $\text{K}^+(\text{aq}) + \text{e}^- \rightarrow \text{K}(\text{s})$   
 $\text{Ca}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Ca}(\text{s})$   
 $\text{Na}^+(\text{aq}) + \text{e}^- \rightarrow \text{Na}(\text{s})$   
 $\text{Mg}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Mg}(\text{s})$   
 $\text{Al}^{3+}(\text{aq}) + 3\text{e}^- \rightarrow \text{Al}(\text{s})$   
 $\text{Mn}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Mn}(\text{s})$   
 $\text{Zn}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Zn}(\text{s})$   
 $\text{Cr}^{3+}(\text{aq}) + 3\text{e}^- \rightarrow \text{Cr}(\text{s})$   
 $\text{Fe}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Fe}(\text{s})$   
 $\text{Co}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Co}(\text{s})$   
 $\text{Ni}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Ni}(\text{s})$   
 $\text{Sn}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Sn}(\text{s})$   
 $\text{Pb}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Pb}(\text{s})$   
 $\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Cu}(\text{s})$   
 $\text{Ag}^+(\text{aq}) + \text{e}^- \rightarrow \text{Ag}(\text{s})$   
 $\text{Au}^+(\text{aq}) + \text{e}^- \rightarrow \text{Au}(\text{s})$

**FIGURE 5.1.9** Reduction half-equations

The metals are listed on the right-hand side of the series, from the least reactive (Pt and Au) at the bottom to the most reactive (K and Na) at the top. The higher up the table a metal is placed, the more reactive it is. Remember that the most reactive metals are those that are oxidised most easily.



Metals, with their small number of valence electrons, generally act as reducing agents. A relatively small amount of energy is required to remove these valence electrons. In general, the lower the amount of energy required to remove the valence electrons, the more readily a metal will act as a reducing agent.

As you go down the reactivity series of metals in Figure 5.1.8:

- the metals, which are on the right-hand side, become less reactive. This means the metals higher in the series are easier to oxidise and therefore stronger reducing agents
- the metal cations, which are on the left-hand side, become increasingly easier to reduce and therefore more reactive. Cations lower in the series have a greater attraction for electrons so they are easier to reduce and are therefore relatively strong oxidising agents.

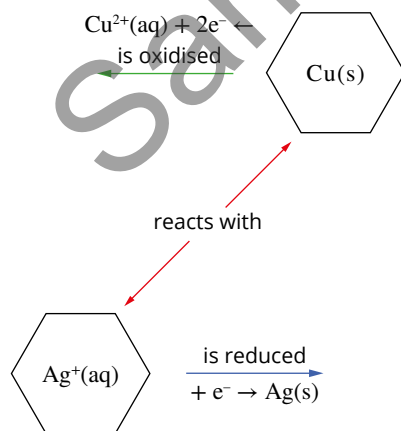
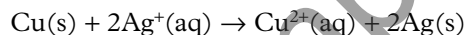
## Metal displacement reactions

The order in which metals and their metal ions appear in the reactivity series enables you to predict which metals will **displace** other metals from solutions of their ions. Such reactions are known as **metal displacement reactions**.

A more reactive metal will be oxidised by, and donate its electrons to, the cation of a less reactive metal. The cation receives the electrons and is reduced. In other words, for a naturally occurring **spontaneous redox reaction** to occur, the metal ions of one metal must be below the other metal in the reactivity series, as shown in Figure 5.1.10. The more reactive metal acts as the reducing agent, and the metal ions of the other metal act as the oxidising agent.

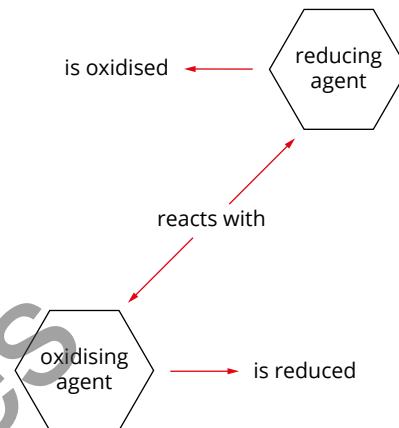
When a strip of copper wire is placed in a solution of silver nitrate as shown in Figure 5.1.11, silver ions are reduced to silver atoms by copper atoms. The silver atoms are deposited as silver crystals. The copper atoms are oxidised to form a blue solution containing copper(II) ions. As a result of the reaction, copper(II) ions have displaced silver ions from the solution.

Silver ions have oxidised copper atoms, consistent with their order in the reactivity series, as shown in Figure 5.1.12. The overall redox reaction can be represented by the equation:



**FIGURE 5.1.12** A spontaneous redox reaction occurs when copper is added to a solution of silver nitrate. Silver ions oxidise copper atoms.

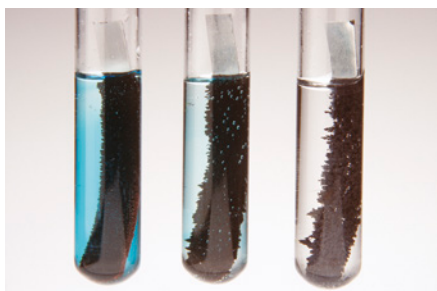
**i** A metal ion lower in the reactivity series (an oxidising agent) will react with a metal higher in the reactivity series (a reducing agent).



**FIGURE 5.1.10** Predicting the reaction between an oxidising agent and a reducing agent



**FIGURE 5.1.11** When a strip of copper wire is suspended in a solution of silver nitrate in the flask on the left, long crystals of silver metal start to form. In the flask on the right, the copper has displaced the silver from the solution.



**FIGURE 5.1.13** A brown deposit of copper metal is observed forming on the zinc and the blue copper(II) sulfate solution gradually becomes colourless as the concentration of  $\text{Cu}^{2+}$  ions decreases.

According to the reactivity series, a metal displacement reaction is predicted to occur when zinc is added to copper(II) sulfate solution, as shown in Figure 5.1.13.

### Worked example 5.1.4

#### PREDICTING METAL DISPLACEMENT REACTIONS

Predict whether zinc will displace copper from a solution containing copper(II) ions and, if appropriate, construct the overall equation for the reaction.

| Thinking  | Working   |
|---|---|
| Locate the metal and the metal ions in the reactivity series.   | Metals (reducing agents) are found on the right-hand side of the reactivity series and metal ions (oxidising agents) are found on the left-hand side of the reactivity series.<br>$\text{Zn}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Zn}(\text{s})$<br>$\text{Cr}^{3+}(\text{aq}) + 3\text{e}^- \rightarrow \text{Cr}(\text{s})$<br>$\text{Fe}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Fe}(\text{s})$<br>$\text{Co}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Co}(\text{s})$<br>$\text{Ni}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Ni}(\text{s})$<br>$\text{Sn}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Sn}(\text{s})$<br>$\text{Pb}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Pb}(\text{s})$<br>$2\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{H}_2(\text{g})$<br>$\text{Sn}^{4+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Sn}(\text{aq})$<br>$\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Cu}(\text{s})$ |
| Determine whether the metal is above (and to the left of) the metal ion in the table. If this is the case, there will be a reaction.                        | You can see from the reactivity series that Zn is on the right-hand side because it is a reducing agent and it is above $\text{Cu}^{2+}$ , so there will be a reaction as shown in Figure 5.1.12.   |
| Show the reduction reaction for the metal ion directly as it is written in the reactivity series, including states.   | $\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Cu}(\text{s})$   |
| Show the oxidation reaction for the metal from the reactivity series, writing the metal on the left-hand side of the arrow (as a reactant). Include states. | $\text{Zn}(\text{s}) \rightarrow \text{Zn}^{2+}(\text{aq}) + 2\text{e}^-$   |
| Combine the two half-equations, balancing electrons, to give the overall equation for the reaction.   | $\text{Zn}(\text{s}) \rightarrow \text{Zn}^{2+}(\text{aq}) + 2\text{e}^-$<br>$\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Cu}(\text{s})$<br><hr style="border-top: 1px dashed black;"/> $\text{Zn}(\text{s}) + \text{Cu}^{2+}(\text{aq}) \rightarrow \text{Zn}^{2+}(\text{aq}) + \text{Cu}(\text{s})$   |

#### ► Try yourself 5.1.4

#### PREDICTING METAL DISPLACEMENT REACTIONS

Predict whether copper will displace silver from a solution containing silver ions and, if appropriate, construct the overall equation for the reaction.

## CORROSION

The reactions that occur when metals corrode are redox reactions. The costs associated with corroding metals are substantial, especially since iron, which is particularly prone to corrosion in the presence of water and oxygen, is so widely used as a structural material for buildings, bridges, gas and water pipes and ships. The effect of corrosion in water pipes is evident in the pumping system shown in Figure 5.1.14.



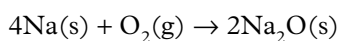
**FIGURE 5.1.14** Corrosion is causing water to leak in these pipes in a pumping system.

In Australia, about \$50 billion (approximately 3% of gross domestic product) is spent each year in an effort to prevent metals from corroding and replacing metal that has corroded. In spite of such efforts, steel structures continue to corrode, eventually producing the familiar orange-brown flakes known as rust, although corrosion prevention methods can slow down the rate of corrosion considerably.

This module will give you an opportunity to consider corrosion in terms of the causes and effects of an issue that relates to redox chemistry. In doing so, you will look at the redox reactions involved in corrosion both in the presence of water and in the absence of water.

### Dry corrosion

Direct reaction with oxygen in the air to form a metal oxide is known as **direct corrosion** or **dry corrosion**. Sodium is so reactive that it must be stored under oil to prevent contact with oxygen. The following equation represents the dry corrosion of sodium:



Dry corrosion of aluminium forms a tough, impervious coating of aluminium oxide ( $\text{Al}_2\text{O}_3$ ), which protects the metal underneath from further contact with oxygen. The aluminium window frame in Figure 5.1.15 is lightweight and corrosion resistant. Therefore it is an excellent material in situations where maintenance would be difficult.

Iron is much less reactive than sodium or aluminium; the rate of dry corrosion of iron is slow at room temperatures. When iron does corrode, it forms a coating that flakes off readily, leaving the metal underneath exposed to further corrosion.



**FIGURE 5.1.15** An aluminium window frame is resistant to corrosion and is a useful material in situations where maintenance would be difficult.

## Wet corrosion

The presence of moisture accelerates the corrosion of iron. This process is known as **wet corrosion**. The best-known example of wet corrosion is the formation of rust as a flaky, brown-red coating on iron.

Wet corrosion can occur in moist air or by direct immersion in water. Several factors affect the rate at which wet corrosion occurs. Consider the observations represented in Figure 5.1.16.



**FIGURE 5.1.16** Wet corrosion. (a) A piece of steel wool (iron) does not corrode on supermarket shelves. However, once it becomes wet through use, it corrodes quickly. (b) An iron barbecue grill that has been coated with grease shows little sign of corrosion, even after being exposed to the rain for some time. (c) Rust in a car generally starts inside door frames, under mudguards, or in places where the paint has been chipped. (d) Shipwrecks corrode rapidly and will eventually disintegrate. (e) Corrosion occurs more rapidly in cities with a pollution problem, particularly where the pollutants include acidic oxides such as nitrogen dioxide and sulfur dioxide.

Each of these observations provides information about the factors that influence the rate of wet corrosion of iron. In general, corrosion is accelerated by:

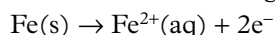
- the presence of water
- impurities such as salt and acidic pollutants that dissolve in the water.

However, corrosion can be reduced when the iron is alloyed with certain other materials or when it has a protective coating. You will see this later when the methods of prevention of corrosion are discussed.

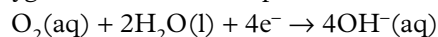
### The wet corrosion process

Rust is a hydrated oxide of iron with the formula  $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ . There can be one to three water molecules associated with the iron oxide in its structure. An understanding of the steps involved in corrosion helps scientists to identify methods of corrosion prevention.

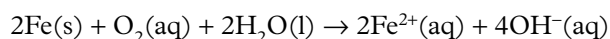
Step 1: Iron is oxidised to form  $\text{Fe}^{2+}$  ions at one region on the iron surface:



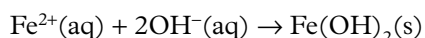
At the same time at another region on the surface, using the electrons produced by the oxidation process, oxygen is reduced in the presence of water to hydroxide ions:



The overall equation for step 1 is:

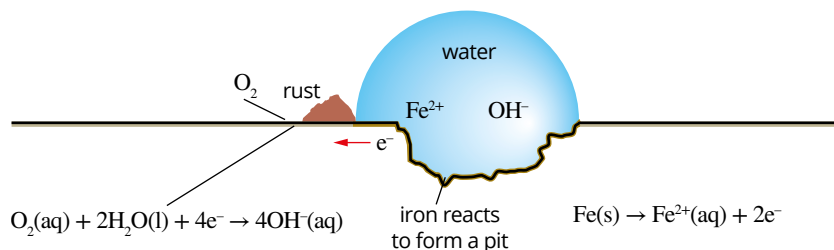


Step 2: The formation of a precipitate of iron(II) hydroxide:



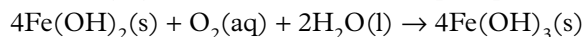


Steps 1 and 2 of the wet corrosion process are summarised in Figure 5.1.17.



**FIGURE 5.1.17** During wet corrosion, electrons are transferred through the iron from the area where oxidation occurs to the area where reduction occurs. Ions flow through the water droplets.

Step 3: Further oxidation of iron(II) hydroxide occurs in the presence of oxygen and water to produce iron(III) hydroxide, a red-brown precipitate:



Step 4: In air, the iron(III) hydroxide loses water to form hydrated iron(III) oxide ( $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ ), which is known as rust.

The porous rust easily flakes off the surface of the iron, exposing the iron underneath to further oxidation.

The wet corrosion of iron is accelerated if the water contains dissolved ions. This is particularly evident in coastal areas where iron objects are exposed to seawater. The presence of dissolved ions in the water increases its conductivity, which results in an increase in the rate of iron corrosion.

## Prevention of corrosion

There are several ways to protect iron and steel structures against corrosion. These depend on the environment in which the structure is located, the design and intended use of the structure, and the relative costs of various protection measures.

The simplest way to protect against corrosion relies on the creation of a barrier between the iron and oxygen and water to provide a surface protection. Other methods are based on an understanding of the electrochemical nature of corrosion.

### Surface protection

Surface protection involves covering the surface of the iron to prevent contact with oxygen and moisture. Materials such as paint and plastic can be used for this purpose. Moving parts, such as a bicycle chain, can be coated with oil or grease to reduce friction and prevent contact with oxygen and moisture.

Iron can also be protected by alloying with small quantities of metals such as chromium, nickel, manganese or molybdenum to produce stainless steel. The atoms of the metals used to make the **alloy** are all bonded into the metallic lattice. These metals oxidise slightly in air, but the oxide coating produced is continuous and unreactive. This oxide layer protects the metal from further oxidation.

Iron and steel can also be coated with thin layers of less reactive metals in a process known as **electroplating**. The ‘tin’ cans used to package food are made from steel plated with tin. Tin is a much less reactive metal than iron and does not corrode greatly in the atmosphere. In addition to the tin coating, cans used for food, such as the ones shown in Figure 5.1.18, have a plastic liner to prevent contact between the food and any metal oxides that may be present.

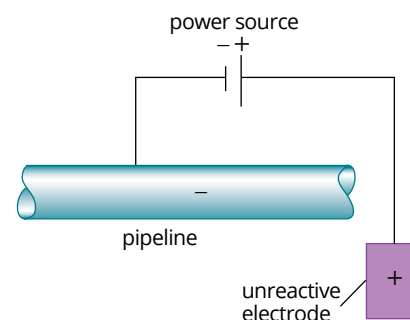
### Electrochemical protection

**Cathodic protection** involves the use of a low-voltage, direct current (DC) power supply to give the iron being protected a negative charge. Because the iron is receiving electrons, oxidation is inhibited. Recall that oxidation is the loss of electrons.

The iron becomes the site of the reduction reaction, and is called the **cathode**. This method, represented in Figure 5.1.19, is used to protect large-scale steel structures such as wharves and pipelines. A single DC source operating at 4.2V and 2.5A will protect many kilometres of pipeline.



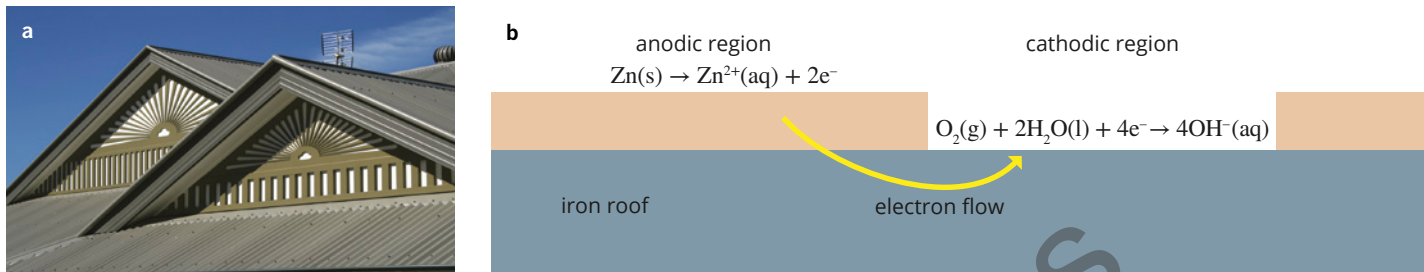
**FIGURE 5.1.18** These food cans are made from steel that has been plated with tin to prevent them from corroding.



**FIGURE 5.1.19** A pipeline carrying natural gas can be protected from corrosion if a direct current source is connected at intervals to give the pipe a negative charge.

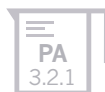
**Sacrificial protection** also involves the iron acting as the cathode. A more easily oxidised metal, such as zinc, forms a region called the **anode** and is ‘sacrificed’ in order to protect the iron from corrosion. The more reactive metal loses electrons and forms metal cations in preference to the iron.

Iron that has been coated in zinc is known as galvanised iron and is used widely for roofs and sheds, as shown in Figure 5.1.20a. Galvanised iron is an example of sacrificial protection. When the zinc coating is scratched, the iron is still protected because the zinc loses electrons more readily than the iron. The diagram in Figure 5.1.20b depicts this process. The zinc slowly corrodes but the iron is protected for years.



**FIGURE 5.1.20** (a) A galvanised iron roof is a common sight in Australia. The zinc coating is oxidised in preference to the iron, protecting the structural role of the iron (b) Diagram showing cathodic and anodic regions.

Underground steel pipelines, bridge pillars and the steel hulls of ships can be protected by connecting them to blocks or plates of zinc, or other more reactive metals such as magnesium, as shown in Figure 5.1.21. Because these metals are more easily oxidised than iron, they lose electrons, which are transferred to the iron where reduction of oxygen and water occurs. The reactive metals, which are called **sacrificial anodes**, are eventually consumed and must therefore be replaced, but this is less expensive than replacing the steel structures that are being protected.



**FIGURE 5.1.21** These aluminium sacrificial anodes are attached to the underwater steel structures of offshore gas platforms to protect them against corrosion.

## 5.1 Review

### SUMMARY

- Redox reactions are electron transfer reactions; one or more reactant substances lose electrons which are accepted by other reactants.
- The loss of electrons by a reactant is known as oxidation; the gain of electrons by a reactant is known as reduction.
- The loss and gain of electrons by reactants occurs simultaneously, so oxidation and reduction processes cannot occur independently of one another.
- Reduction processes and oxidation processes can each be represented via half-equations; the sum of the reduction and oxidation half-equations is used to generate the full redox equation.
- Oxidising agents cause the oxidation of another substance—they are themselves reduced in redox reactions; reducing agents cause the reduction of other substances—they are themselves oxidised in redox reactions.
- The relative reactivity of metals is represented in the metal reactivity series.
  - The metal reactivity series lists half-equations involving metals and their corresponding cations.
  - The half-equations involving stronger oxidising agents (the ones more easily reduced) appear lower in the reactivity series than those involving weaker oxidising agents.
  - The reactivity series can be used to predict whether a redox reaction is likely to occur.
- Metal displacement reactions involve the transfer of electrons from a more reactive metal to the positive ions of a less reactive metal in solution.
- Some metals readily corrode via oxidation processes. These processes can be characterised as 'dry corrosion' or 'wet corrosion'.
  - Dry corrosion refers to the oxidation of a metal by oxygen gas.
  - Wet corrosion involves both oxygen gas and water.
- Corrosion of metals can be prevented in a number of ways including:
  - surface protection (via paints, plastics and electroplating methods); or by
  - electrochemical protection (via cathodic protection or the use of sacrificial anodes).

### KEY QUESTIONS

#### Retrieval

- 1 Define the following terms.
  - a oxidation
  - b reduction
  - c redox reaction
- 2 Describe:
  - a an oxidising agent
  - b a reducing agent.
- 3 Use Figure 5.1.8 on page 124 to list the following in terms of increasing reducing strength: Mg, Ag, Ni, Sn, Li and Cu
- 4 State the difference between wet corrosion and dry corrosion.
- 5 Identify each of the following half-equations as involving either oxidation or reduction.
  - a  $\text{Na(s)} \rightarrow \text{Na}^+(\text{aq}) + \text{e}^-$
  - b  $\text{Cl}_2(\text{g}) + 2\text{e}^- \rightarrow 2\text{Cl}^-(\text{aq})$
  - c  $\text{S(s)} + 2\text{e}^- \rightarrow \text{S}^{2-}(\text{aq})$
  - d  $\text{Zn(s)} \rightarrow \text{Zn}^{2+}(\text{aq}) + 2\text{e}^-$

#### Comprehension

- 6 Summarise redox reactions by using the following terms to complete the sentences: gains, loses,  $\text{I}_2$ ,  $\text{I}^-$ , reduced, oxidised.

When a reducing agent, such as Fe, reacts with an oxidising agent, such as \_\_\_\_\_, an ionic compound is formed. The reducing agent \_\_\_\_\_ electrons (is \_\_\_\_\_) and at the same time the oxidising agent \_\_\_\_\_ electrons (is \_\_\_\_\_). In this case, the products are  $\text{Fe}^{2+}$  and \_\_\_\_\_, which form  $\text{FeI}_2$ .
- 7 Explain why iron corrosion occurs more rapidly near coastal environments.

#### Analysis

- 8 Determine why underwater steel pillars often corrode more rapidly just beneath the surface of the water than above.

*continued over page*

## 5.1 Review *continued*

- 9** When a strip of magnesium metal is placed in a blue solution containing copper(II) ions ( $\text{Cu}^{2+}(\text{aq})$ ), crystals of copper appear and the solution soon becomes paler in colour.
- Show that this reaction is a redox reaction by identifying the substance that is oxidised and the one that is reduced.
  - Construct a half-equation for the oxidation reaction.
  - Construct a half-equation for the reduction reaction.
  - Construct an overall redox equation.
  - Identify the oxidising agent and the reducing agent.
  - Explain why the solution loses some of its blue colour as a result of the reaction.
- 10** Refer to the reactivity series of metals on page 124 to predict whether the following reactions will spontaneously occur.
- Silver metal is placed in a copper(II) nitrate solution.
  - A strip of aluminium is placed in a sodium chloride solution.
  - Magnesium is added to a solution of iron(II) sulfate.
  - Zinc is placed in a tin(II) sulfate solution.
  - A piece of tin is placed in a silver nitrate solution.
  - Lead(II) nitrate solution is poured into a beaker containing zinc granules.
  - Gold foil is added to a lead(II) nitrate solution.
- 11** Use the reactivity series of metals on page 124 to predict whether a reaction will occur in each of the following situations. Construct an overall equation for each reaction that you predict will occur.
- Copper(II) sulfate solution is stored in an aluminium container.
  - Sodium chloride solution is stored in a copper container.
  - Silver nitrate solution is stored in a zinc container.
- 12** Balance the following half-equations and then classify each as an oxidation or a reduction reaction.
- $\text{Fe}(\text{s}) \rightarrow \text{Fe}^{3+}(\text{aq})$
  - $\text{K}(\text{s}) \rightarrow \text{K}^{+}(\text{aq})$
  - $\text{F}_2(\text{g}) \rightarrow \text{F}^{-}(\text{aq})$
  - $\text{O}_2(\text{g}) \rightarrow \text{O}^{2-}(\text{aq})$

Sample pages



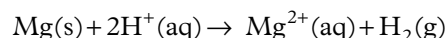
## 5.2 Identifying redox reactions

### BY THE END OF THIS MODULE YOU SHOULD BE ABLE TO:

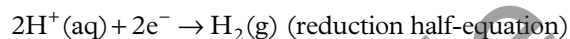
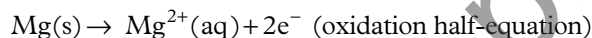
- assign oxidation numbers to atoms in elements, compounds and polyatomic ions
- use oxidation numbers to determine whether a reaction is a redox reaction
- understand oxidation and reduction in terms of changes in oxidation numbers of atoms
- use oxidation numbers to identify oxidising and reducing agents
- use oxidation numbers to name ionic compounds involving transition metal ions
- use oxidation numbers to identify conjugate redox pairs.



How can we tell if a particular chemical reaction is in fact a redox reaction? In the reaction of magnesium ( $\text{Mg(s)}$ ) with hydrochloric acid ( $\text{HCl(aq)}$ ) we can see that charges on the  $\text{Mg(s)}$  and  $\text{H}^{\text{+}}(\text{aq})$  ions change during the reaction. The net ionic equation for this reaction is:



The individual half-equations can be represented as:

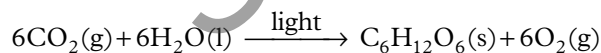


Clearly there is a transfer of electrons from the magnesium metal to the  $\text{H}^{\text{+}}$  ions, which changes the charge on both species. This change in charge is indicative of a redox reaction.

But what about a combustion reaction? For example, the combustion of methane ( $\text{CH}_4$ ):



Or consider photosynthesis, which can be represented by this overall chemical equation:



Are these redox reactions? The substances represented in each of these equations are all molecular substances and have no net charge. We cannot say by simple inspection that there has been a change in charge of any of the atoms involved and we cannot readily determine if electron transfer has occurred. Therefore, we cannot easily determine if these reactions are redox reactions.

### OXIDATION NUMBERS

It turns out that the combustion and photosynthesis reactions shown above are redox reactions and that a transfer of electrons has occurred between atoms of the reactant molecules. So the question remains; how can we tell if a chemical reaction is a redox reaction? And how can we tell which atom or molecule has been oxidised (and is therefore the reducing agent), and which atom or molecule has been reduced (and is therefore the oxidising agent)?

We do this by assigning **oxidation numbers** to atomic species or to individual atoms within molecular species. The oxidation number of an atom in a substance represents the charge that an atom would have if it was an ion.

The key to identifying whether a chemical reaction is a redox reaction is to determine if the oxidation number of any atoms change during the course of a reaction.

## Rules for assigning oxidation numbers

Oxidation numbers are also referred to as **oxidation states**. The rules for assigning oxidation numbers (or states) to atoms in substances are outlined in Table 5.2.1. In the examples shown in the table, the oxidation number of an element is placed above its symbol. The plus or minus sign precedes the number and so distinguishes the oxidation number from the charge on an ion where the sign is generally placed after the number. For example, the oxide ion ( $O^{2-}$ ) has a charge of  $2-$  and an oxidation number of  $-2$ . While the values are the same in this instance, it is important to remember that oxidation states do not always indicate a charge on the species.

**i** If the oxidation number of a particular atom changes during a chemical reaction then we can say that the atom has undergone oxidation or reduction and that the reaction, overall, is a redox reaction.

**TABLE 5.2.1** Rules for determining oxidation numbers of elements in compounds

| Rule  | Examples   |
|---|--|
| 1 The oxidation number of a free element is zero.   | $\overset{0}{\text{Na}}, \overset{0}{\text{C}}, \overset{0}{\text{Cl}_2}, \overset{0}{\text{P}_4}$   |
| 2 The oxidation number of a simple ion is equal to the charge on the ion.   | $\overset{+1}{\text{Na}^+}, \overset{-1}{\text{Cl}^-}, \overset{+2}{\text{Mg}^{2+}}, \overset{-2}{\text{O}^{2-}}, \overset{+3}{\text{Al}^{3+}}, \overset{-3}{\text{N}^{3-}}$   |
| 3 In compounds, some elements have oxidation numbers that are regarded as fixed, except in a few exceptional circumstances.   |  |
| a Main group metals have an oxidation number equal to the charge on their ions.   | ionic compounds: $\overset{+1}{\text{KCl}}, \overset{+2}{\text{MgSO}_4}$   |
| b Hydrogen has an oxidation number of $+1$ when it forms compounds with non-metals.<br>Exception: In metal hydrides, the oxidation number of hydrogen is $-1$ .   | compounds of H: $\overset{+1}{\text{H}_2\text{O}}$<br>metal hydrides: $\overset{-1}{\text{NaH}}, \overset{-1}{\text{CaH}_2}$   |
| c Oxygen usually has an oxidation number of $-2$ .<br>Exceptions:<br>In compounds with fluorine, oxygen has a positive oxidation number.<br>In peroxides, oxygen has an oxidation number of $-1$ .  | compounds of O: $\overset{-2}{\text{H}_2\text{O}}$<br>compounds of O and F: $\overset{+2}{\text{OF}_2}$<br>peroxides: $\overset{-1}{\text{H}_2\text{O}_2}, \overset{-1}{\text{BaO}_2}$   |
| d Halogens: The oxidation number of fluorine is $-1$ in all of its compounds. The oxidation number of the other halogens in their compounds (i.e. Cl, Br, I) is also $-1$ except where they are involved in compounds with O or another halogen above them in Group 17 in the periodic table. | fluorine compounds: $\overset{+1}{\text{HF}}, \overset{+2}{\text{OF}_2}$<br>other halogen compounds: $\overset{+1}{\text{HCl}}, \overset{+1}{\text{Cl}_2\text{O}}, \overset{+5}{\text{ClF}_5}$   |
| 4 The sum of the oxidation numbers of all atoms in a neutral compound is zero.  | $\overset{+4}{\text{C}}\overset{-2}{\text{O}_2}$<br>Note that in $\text{CO}_2$ , the oxidation number of each oxygen atom is written as $-2$ ; since the sum of all atoms must equal zero for a neutral compound then we can easily calculate that the oxidation number for the single C atom must be 4. |
| 5 The sum of the oxidation numbers of all atoms in a polyatomic ion is equal to the charge on the ion.  | $\overset{+6}{\text{S}}\overset{-2}{\text{O}_4}{}^{2-}, \overset{-3}{\text{N}}\overset{+1}{\text{H}_4}{}^+$  |
| 6 The most electronegative element is assigned the negative oxidation number.   | $\overset{+2}{\text{O}}\overset{-1}{\text{F}_2}, \overset{+6}{\text{S}}\overset{-1}{\text{F}_6}$   |

Oxidation numbers have no physical meaning and they do not indicate a formal charge nor are they representative of the physical or chemical properties of the substance. However, they are a useful tool for identifying which atoms have been oxidised and which atoms have been reduced.

## Calculating oxidation numbers of atoms in compounds

The common oxidation states of the first 32 elements in their compounds are shown in the periodic table in Figure 5.2.1. Transition metals and some non-metals can have a range of oxidation states. These are usually calculated after applying the rules for all other elements in the compound.

**i** If the oxidation number of an atom has increased after a chemical reaction, that atom has undergone oxidation.

If the oxidation number of an atom has decreased after a chemical reaction, that atom has undergone reduction.

| 1                           | 2                            | 3                           | 4                           | 5                           | 6                            | 7                             | 8                       | 9                         | 10                        | 11                        | 12                      | 13                           | 14                            | 15                            | 16                           | 17                           |
|-----------------------------|------------------------------|-----------------------------|-----------------------------|-----------------------------|------------------------------|-------------------------------|-------------------------|---------------------------|---------------------------|---------------------------|-------------------------|------------------------------|-------------------------------|-------------------------------|------------------------------|------------------------------|
| 1<br><b>H</b><br>hydrogen   |                              |                             |                             |                             |                              |                               |                         |                           |                           |                           |                         |                              |                               |                               |                              |                              |
| 3<br><b>Li</b><br>lithium   | 4<br><b>Be</b><br>beryllium  |                             |                             |                             |                              |                               |                         |                           |                           |                           |                         | 5<br><b>B</b><br>boron       | 6<br><b>C*</b><br>carbon      | 7<br><b>N*</b><br>nitrogen    | 8<br><b>O</b><br>oxygen      | 9<br><b>F</b><br>fluorine    |
| 11<br><b>Na</b><br>sodium   | 12<br><b>Mg</b><br>magnesium |                             |                             |                             |                              |                               |                         |                           |                           |                           |                         | 13<br><b>Al</b><br>aluminium | 14<br><b>Si*</b><br>silicon   | 15<br><b>P*</b><br>phosphorus | 16<br><b>S*</b><br>sulfur    | 17<br><b>Cl*</b><br>chlorine |
| 19<br><b>K</b><br>potassium | 20<br><b>Ca</b><br>calcium   | 21<br><b>Sc</b><br>scandium | 22<br><b>Ti</b><br>titanium | 23<br><b>V*</b><br>vanadium | 24<br><b>Cr*</b><br>chromium | 25<br><b>Mn*</b><br>manganese | 26<br><b>Fe</b><br>iron | 27<br><b>Co</b><br>cobalt | 28<br><b>Ni</b><br>nickel | 29<br><b>Cu</b><br>copper | 30<br><b>Zn</b><br>zinc | 31<br><b>Ga</b><br>gallium   | 32<br><b>Ge*</b><br>germanium | 33<br><b>As*</b><br>arsenic   | 34<br><b>Se*</b><br>selenium | 35<br><b>Br*</b><br>bromine  |

+1 oxidation state       +2 oxidation state       -2 oxidation state  
 +3 oxidation state       range of oxidation states possible

FIGURE 5.2.1 Part of the periodic table showing the most common oxidation states of some elements.

For a compound containing several elements, you can use algebra and the rules given in Table 5.2.1 to calculate the oxidation number of an element.

### Worked example 5.2.1

#### CALCULATING OXIDATION NUMBERS

|  |  |
|--|--|
| Use the rules in Table 5.2.1 on page 134 to determine the oxidation number of each element in potassium perchlorate ( $\text{KClO}_4$ ). |  |
| <b>Thinking</b>  | <b>Working</b>   |
| Identify an element that has a set value.  | K is a main group metal in group 1.<br>Applying rule 3a, the oxidation number of potassium is +1.  |
| Identify any other elements that have set values.  | According to rule 3c, oxygen has an oxidation number of -2 unless attached to fluorine or in a peroxide.   |
| Use algebra to work out the oxidation number of other elements.  | Let the oxidation number of chlorine in $\text{KClO}_4$ be $x$ .<br>Solve the sum of the oxidation numbers for $x$ :<br>$+1 + x + (4 \times -2) = 0$ $+1 + x - 8 = 0$ $x - 7 = 0$ $x = +7$   |
| Show oxidation numbers above the elements in the formula.  | $^{+1} \text{K} ^{-2} \text{ClO}_4$<br>Note that the oxidation number of oxygen is written as -2 (not as -8), even though there are four oxygen atoms in the formula.<br>Confirming rule 4 from Table 5.2.1 we can see that the sum of oxidation numbers of all atoms in the compound is zero (i.e. $1 + 7 + 4 \times -2 = 0$ ). |

## ► Try yourself 5.2.1

### CALCULATING OXIDATION NUMBERS

Use the rules in Table 5.2.1 on page 134 to determine the oxidation number of each element in sodium nitrate ( $\text{NaNO}_3$ ).

### USING OXIDATION NUMBERS

The oxidation number concept is a valuable tool that can be used to:

- identify whether a chemical reaction is a redox reaction (remember, if there is no change of oxidation number for all atoms involved in the reaction, excluding spectator ions, then the reaction is not a redox reaction)
- determine which substance is the oxidising agent and which is the reducing agent
- name ionic compounds involving cations derived from transition metals
- identify conjugate redox pairs.

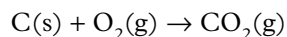
### Using oxidation numbers to identify oxidising and reducing agents

We have already noted that a change in oxidation number of an atom after a chemical reaction indicates that the reaction is a redox reaction. We also know that:

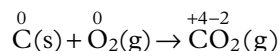
- an increase in oxidation number of an atom means that the atom has been oxidised; and
- a decrease in oxidation number of an atom means that the atom has been reduced.

Finally, we also know that an oxidising agent is itself reduced, and that a reducing agent is itself oxidised. We can therefore use this knowledge to assist in determining which reactant is the oxidising agent and which reactant is the reducing agent.

At the beginning of this chapter, you were alerted to a number of everyday processes that are redox reactions. Combustion reactions, where fuel is burned in order to produce heat while giving off  $\text{CO}_2$  and water, are examples of redox reactions that are very important in our society. The equation for the burning of carbon in excess oxygen is:



At first glance, the reaction may not seem like a redox reaction because none of the species are ionic compounds so it is not clear which reactant is losing or gaining electrons. By using oxidation numbers, we can identify both an oxidation process and a reduction process for the reaction:



The carbon is oxidised because its oxidation number increases from 0 to +4, and the oxygen is reduced because its oxidation number decreases from 0 to -2. Furthermore, since the carbon is oxidised, it is identified as the reducing agent—it has enabled, or caused, the reduction of oxygen. Similarly, since oxygen has been reduced, it is identified as the oxidising agent—it has enabled, or caused, the oxidation of carbon.

In this way, the use of oxidation numbers allows you to look at a chemical reaction and determine whether it is a redox reaction and then, more specifically, to determine which reactant is the oxidising agent and which is the reducing agent.



## Worked example 5.2.2

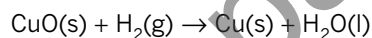
### USING OXIDATION NUMBERS TO IDENTIFY OXIDISING AND REDUCING AGENTS

|  |   |
|--|---|
| Determine whether the following is a redox reaction and (if so) identify the oxidising and reducing agents:<br>$\text{CH}_4(\text{g}) + 2\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l})$ |   |
| <b>Thinking</b>  | <b>Working</b>  |
| Determine the oxidation numbers for each element in the equation.  | $\overset{-4}{\text{C}}\overset{+1}{\text{H}}_4(\text{g}) + \overset{0}{\text{O}}_2(\text{g}) \rightarrow \overset{+4}{\text{C}}\overset{-2}{\text{O}}_2(\text{g}) + 2\overset{+1}{\text{H}}\overset{-2}{\text{O}}(\text{l})$   |
| Assess if the oxidation number of any element has changed. If so, identify if it has increased (oxidation) or decreased (reduction).   | The oxidation number of C has increased from $-4$ to $+4$ , so the carbon in $\text{CH}_4$ has been oxidised. The oxidation number of O has decreased from $0$ to $-2$ , so oxygen has been reduced. The oxidation number for H has remained unchanged, so hydrogen has not undergone oxidation or reduction. |
| The compound or element containing the atom that has been oxidised is designated as the reducing agent.<br>The compound or element containing the atom that has been reduced is designated as the oxidising agent.               | $\text{CH}_4$ is identified as the reducing agent (it caused the reduction of $\text{O}_2$ ) and $\text{O}_2$ has been identified as the oxidising agent (it caused the oxidation of $\text{CH}_4$ ).   |

### ► Try yourself 5.2.2

### USING OXIDATION NUMBERS TO IDENTIFY OXIDISING AND REDUCING AGENTS

Determine whether the following is a redox reaction and (if so) identify the oxidising and reducing agents:



## Using oxidation numbers to name ionic compounds

As you learnt in Units 1 and 2, **transition elements** can form ions with a number of different charges. This means that many transition metals have variable oxidation numbers (or oxidation states). For example, there are two compounds that can be called iron chloride:  $\text{FeCl}_2$  and  $\text{FeCl}_3$ .

Using the rules in Table 5.2.1 on page 134, you can see that the chloride ion has an oxidation number of  $-1$ . In  $\text{FeCl}_2$  this means the oxidation number of iron is  $+2$ , whereas in  $\text{FeCl}_3$  the oxidation number is  $+3$ .

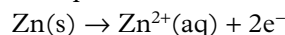
To distinguish between the two iron chlorides, we insert Roman numerals to represent the appropriate oxidation number in the name:

- $\text{FeCl}_2$  is more correctly named iron(II) chloride
- $\text{FeCl}_3$  is more correctly named iron(III) chloride.

## Using oxidation numbers to identify conjugate redox pairs

When a half-equation is written for an oxidation reaction, the reactant, a reducing agent, loses electrons. The product is an oxidising agent. We refer to the reactant and the product that it forms as a **conjugate redox pair**.

For example, consider the half-equation for the oxidation of zinc:



Zinc metal ( $\text{Zn}$ ) is a reducing agent and forms  $\text{Zn}^{2+}(\text{aq})$ , which is an oxidising agent.  $\text{Zn}(\text{s})$  and  $\text{Zn}^{2+}(\text{aq})$  form a conjugate redox pair  $\text{Zn}(\text{s})/\text{Zn}^{2+}(\text{aq})$ .

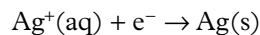
In the  $\text{Zn}(\text{s})/\text{Zn}^{2+}(\text{aq})$  conjugate redox pair, the oxidation number of zinc increases from  $0$  to  $+2$ . The increase in the oxidation number of zinc indicates that it is an oxidation half-reaction.

For the reduction half-equation, the reactant is an oxidising agent and will gain electrons. The product formed is a reducing agent. Therefore, another conjugate redox pair is present in the redox reaction.

**i** For elements that can have variable oxidation states, the use of a Roman numeral in the name indicates the specific oxidation state of the element.

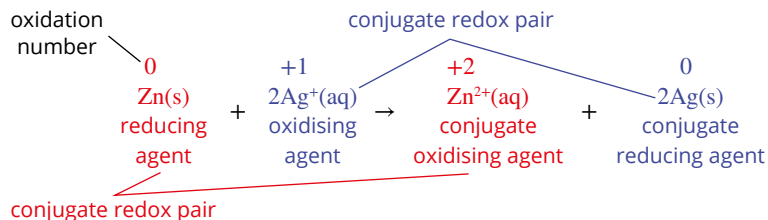
**i** When listing conjugate redox pairs, it is best to include the states of both the oxidising and reducing agent.

For example, consider the half-equation for the reduction of  $\text{Ag}^+(\text{aq})$ :



$\text{Ag}^+(\text{aq})$  is an oxidising agent and forms  $\text{Ag}(\text{s})$ , which is a reducing agent.  $\text{Ag}^+(\text{aq})$  and  $\text{Ag}(\text{s})$  are also a conjugate redox pair. In this case, the oxidation number of silver decreases from +1 to 0, indicating that this is a reduction half-equation.

The relationship between changes in oxidation numbers and conjugate redox pairs can be seen by following the colour-coding in the equation in Figure 5.2.2. One conjugate redox pair is red and the other one is blue.



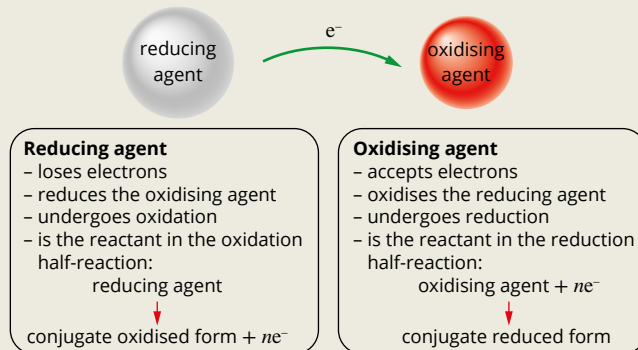
**FIGURE 5.2.2** The change in oxidation numbers seen in conjugate redox pairs. For each redox reaction, there are two conjugate redox pairs.

## 5.2 Review

### SUMMARY

- Oxidation numbers are calculated according to a set of rules, including:
  - free elements have an oxidation number of 0
  - in ionic compounds composed of simple ions, the oxidation number is equal to the charge on the ion
  - hydrogen in a compound usually has an oxidation number of +1
  - oxygen in a compound usually has an oxidation number of -2
  - the sum of the oxidation numbers in a neutral compound is 0
  - the sum of the oxidation numbers in a polyatomic ion is equal to the charge on the ion.
- An increase in the oxidation number of an element in a reaction indicates oxidation has occurred.
- A decrease in the oxidation number of an element in a reaction indicates reduction has occurred.
- For oxidation to occur, there must be a corresponding reduction.
- If there is no change in the oxidation number of any atoms involved in the equation for a particular reaction, then that reaction is not a redox reaction.
- The oxidation number (or oxidation state) is used to name ionic compounds containing transition metal ions. (N.B. the Roman numeral representation of the oxidation number is used.)
- A conjugate redox pair consists of an oxidising agent (a reactant) and the reducing agent (a product) that is formed when the oxidising agent gains electrons. In a redox reaction, if a conjugate redox pair consists of an oxidising agent (the reactant) and the reducing agent that is the product formed when the oxidising agent gains electrons, then the oxidation number of the oxidising agent (the reactant) decreases.
- In a redox reaction, if a conjugate redox pair consists of a reducing agent (a reactant) and the oxidising agent that is the product formed when the reducing agent loses electrons, then the oxidation number of the reducing agent (the reactant) increases.
- Figure 5.2.3 summarises the redox terms that you need to understand from this module.

oxidation number increases      oxidation number decreases



**FIGURE 5.2.3** Summary of redox reaction terms

## KEY QUESTIONS

### Retrieval

- 1 Define the oxidation number of an atom in a substance.
- 2 State the oxidation number of:
  - a an element
  - b a monatomic ion.
- 3 Deduce the correct missing term by completing the following statements using either 'decreases' or 'increases'.
  - a If the oxidation number of an atom \_\_\_\_\_ after a chemical reaction, that atom has undergone oxidation.
  - b If the oxidation number of an atom \_\_\_\_\_ after a chemical reaction, that atom has undergone reduction.
- 4 Determine the oxidation state of the transition metal ion in the following ionic compounds.
  - a copper(I) chloride (CuCl)
  - b iron(III) nitrate (Fe(NO<sub>3</sub>)<sub>3</sub>)
  - c chromium(III) oxide (Cr<sub>2</sub>O<sub>3</sub>)
- 5 Determine which one or more of the following substances contain manganese in the +6 oxidation state: MnCl<sub>2</sub>, MnCl<sub>3</sub>, MnO<sub>2</sub>, KMnO<sub>4</sub>, K<sub>2</sub>MnO<sub>4</sub>.

### Comprehension

- 6 Calculate the oxidation numbers of each element in the following compounds or ions.
  - a CaO
  - b CaCl<sub>2</sub>
  - c HSO<sub>4</sub><sup>-</sup>
  - d MnO<sub>4</sub><sup>-</sup>
  - e F<sub>2</sub>
  - f SO<sub>3</sub><sup>2-</sup>
  - g NaNO<sub>3</sub>
  - h K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>

- 7 Indicate the correct conjugate redox pairs for each redox reaction by completing the following table.

| Redox reaction   | Conjugate redox pair (oxidation process) | Conjugate redox pair (reduction process) |
|--|--|--|
| Na(s) + Ag <sup>+</sup> (aq) → Na <sup>+</sup> (aq) + Ag(s)              |  |  |
| Zn(s) + Cu <sup>2+</sup> (aq) → Zn <sup>2+</sup> (aq) + Cu(s)            |  |  |
| 2K(s) + Cl <sub>2</sub> (g) → 2K <sup>+</sup> (s) + 2Cl <sup>-</sup> (s) |  |  |

### Analysis

- 8 Calculate the oxidation number of carbon in the following.
  - a CO
  - b CO<sub>2</sub>
  - c CH<sub>4</sub>
  - d C (graphite)
  - e HCO<sub>3</sub><sup>-</sup>
- 9 Compare oxidation numbers of atoms on both sides of the following equations to identify the oxidising agents and reducing agents.
  - a Mg(s) + Cl<sub>2</sub>(g) → MgCl<sub>2</sub>(s)
  - b 2SO<sub>2</sub>(g) + O<sub>2</sub>(g) → 2SO<sub>3</sub>(g)
  - c Fe<sub>2</sub>O<sub>3</sub>(s) + 3CO(g) → 2Fe(s) + 3CO<sub>2</sub>(g)
  - d 2Fe<sup>2+</sup>(aq) + H<sub>2</sub>O<sub>2</sub>(aq) + 2H<sup>+</sup>(aq) → 2Fe<sup>3+</sup>(aq) + 2H<sub>2</sub>O(l)
- 10 Each of the following half-equations have a mistake in them. For each half-equation determine what the error is and then state the correct half-equation.
  - a Ag(s) + e<sup>-</sup> → Ag<sup>+</sup>(aq)
  - b Cu(s) + e<sup>-</sup> → Cu<sup>2+</sup>(aq) + 3e<sup>-</sup>
  - c Zn(aq) → Zn<sup>2+</sup>(s) + 2e<sup>-</sup>
  - d I<sub>2</sub>(aq) + e<sup>-</sup> → I<sup>-</sup>(aq)
  - e Na<sup>+</sup>(aq) - e<sup>-</sup> → Na(s)
- 11 The element vanadium can exist in five oxidation states. Arrange V<sup>2+</sup>, V, VO<sub>2</sub><sup>+</sup>, V<sup>3+</sup> and VO<sup>2+</sup> in order of increasing oxidation state.

## 5.3 Balancing complex redox reactions using half-equations



BY THE END OF THIS MODULE YOU SHOULD BE ABLE TO:

- ▶ balance half-equations for complex redox reactions
- ▶ balance overall redox equations for complex reactions.



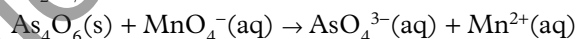
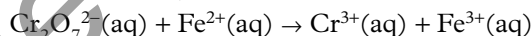
**FIGURE 5.3.1** The 'elephant's toothpaste' demonstration involves a redox reaction in which hydrogen peroxide is both the reducing agent and the oxidising agent.

Not all oxidation and reduction half-equations involve simple ions and their elements. Many interesting redox reactions, such as the 'elephant's toothpaste' reaction shown in Figure 5.3.1, can be quite complicated. For example, they often contain numerous reactants and products, have large stoichiometric coefficients, and typically involve polyatomic ions and other reactants and products that have oxygen and hydrogen in their formulas. The overall balanced equation for this example is  $\text{H}_2\text{O}_2(\text{aq}) + \text{H}_2\text{O}_2(\text{aq}) \rightarrow 2\text{H}_2\text{O}(\text{l}) + \text{O}_2(\text{g})$ . Determining the individual half-equations for reactions like this can be quite complex. In this reaction, a solid potassium iodide catalyst is added to a hydrogen peroxide solution. Red colouring has been added for effect.

In this module you will learn how to balance complex redox equations in a few short steps.

### BALANCING REDOX EQUATIONS FOR COMPLEX REACTIONS

The methods used for balancing chemical equations may break down when dealing with complex redox equations. Consider the following unbalanced chemical equations:



Attempting to balance these equations using the approaches outlined in Units 1 and 2 would not be suitable. For a start, it is not immediately obvious if either of these reactions is a redox reaction; and if they are, it's not clear which substances are undergoing oxidation and which substances are undergoing reduction.

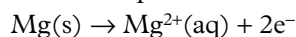
The first of these equations is particularly interesting as the element oxygen does not even appear on the right-hand side of the equation despite being present on the left-hand side. Finally, both of these equations contain complex, polyatomic, oxy-anions, which usually require special attention when balancing equations.

For these reasons, there is a different approach to balancing complex chemical equations using a combination of assigning oxidation numbers and using half-equations. While you have some experience in balancing simple half-equations you need to be able to tackle more complex half-equations before attempting to balance full redox equations.

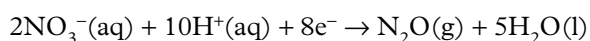
You will first learn how to balance more complex half-equations and then you will learn how to balance full redox equations. In both cases only reactions in acidic conditions are considered.

### Steps for balancing complex half-equations (acidic conditions)

Half-equations that involve atoms or simple ions can be written quite easily. For example, knowing that magnesium metal is oxidised to form  $\text{Mg}^{2+}$  ions in solution, you can readily show the half-equation as:



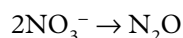
However, half-equations involving polyatomic ions are usually less obvious. The anaesthetic nitrous oxide or laughing gas ( $\text{N}_2\text{O}$ ) can be prepared by the reduction of nitrate ions in an acidic solution:





Such equations can be deduced from the following steps. The reduction of nitrate ions will be used to illustrate this process.

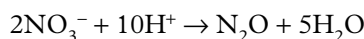
- 1 Balance all elements except oxygen and hydrogen in the half-equation. Since the compound of N on the right-hand side is  $\text{N}_2\text{O}$ , we need two  $\text{NO}_3^-$  ions on the left-hand side:



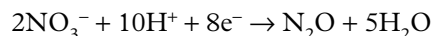
- 2 Balance the oxygen atoms by adding  $\text{H}_2\text{O}$  molecules to one side of the half-equation. Since there are now six O atoms on the left-hand side, we need to put five  $\text{H}_2\text{O}$  molecules on the right-hand side to balance the O atoms:



- 3 Balance the hydrogen atoms by adding  $\text{H}^+$  ions to one side of the half-equation. Since there are now 10 H atoms on the right-hand side, we need to put 10  $\text{H}^+$  ions on the left-hand side:

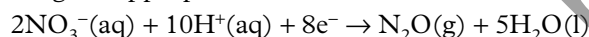


- 4 Balance the charge on both sides of the half-equation by adding electrons ( $\text{e}^-$ ) to the side with the greater positive charge. In this case, the total charge on the left-hand side is  $(2 \times -1) + (10 \times +1) = +8$ . The total charge on the right-hand side is zero. Make the charges equal by adding eight electrons to the left-hand side:



The total charge on both sides is now equal and the total number (and type) of atoms is also equal. This half-equation is now balanced.

- 5 Indicate whether each substance exists as a dissolved solute or as a solid, liquid or gas by inserting the appropriate label:



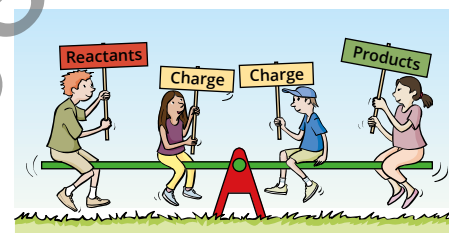
It is important to note that half-equations and full redox equations must be fully balanced, as shown in Figure 5.3.2. The number of each element must be equal on each side, just as with any other chemical equation. In addition, the total charge on each side of the equation must also be equal. We should also note that the charges being equal does not mean they must be zero.

## Steps for balancing full redox equations (acidic conditions)

The steps we use to balance chemical equations for complex redox reactions are outlined below. The five steps for balancing half-equations have been included in Step 3 below.

Balancing complex redox equations is best demonstrated via examples; the unbalanced equations introduced at the beginning of this module are used as examples below.

- 1 Calculate oxidation numbers of each atom to determine which (if any) atoms are undergoing oxidation and which atoms are undergoing reduction. (If no atoms change their oxidation number then the reaction is not a redox reaction and the use of the half-equation approach is not valid.)
- 2 Split the chemical equation into two unbalanced half-equations, one containing the reactants and products for the oxidation process and one containing the reactants and products for the reduction process.
- 3 Construct and balance each half-equation. They must be both mass-balanced and charge-balanced.
  - i Balance all atoms except O and H first.
  - ii Balance O atoms by adding  $\text{H}_2\text{O}$  to one side of the half-equation.
  - iii Balance H atoms by adding  $\text{H}^+$  ions to one side of the equation.
  - iv Balance the charge on both sides of the half-equation by adding electrons ( $\text{e}^-$ ) to the side with the greater positive charge.
  - v Indicate whether each substance exists as a dissolved solute or as a solid, liquid or gas.

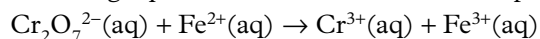


**FIGURE 5.3.2** In balanced half-equations and overall redox equations, the number of atoms of each element is equal on both sides and the total charge on each side is equal.

**i** The steps for balancing complex redox half-equations must be carried out in sequence for the process to work.

- 4 Add the two half-equations together to obtain the final balanced redox equation.
  - i Electrons cannot appear in the final redox equation. If there are unequal numbers of electrons in the half-equations, multiply each half-equation by whole numbers to ensure that the electrons lost in the oxidation half-equation equal the electrons gained in the reduction half-equation.
  - ii Simplify the redox equation by cancelling any species that occurs on both sides.
  - iii Check that you have the same number of each type of atom on each side and check that the total charge on the left-hand side is the same as the total charge on the right-hand side.

To balance the following equation we need to follow the steps outlined above.



Step 1: Calculating the oxidation numbers for each atom using the rules in Table 5.2.1 gives the following for the left-hand side (LHS) and the right-hand side (RHS) of the equation:

LHS: Cr = +6 (rule 5); O = -2 (rule 3c); Fe = +2 (rule 2)

RHS: Cr = +3 (rule 2); Fe = +3 (rule 2)

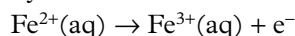
The Fe atom has increased its oxidation number and has therefore undergone oxidation; Cr has decreased its oxidation number and has therefore undergone reduction.

Step 2: Split the reaction into unbalanced oxidation and reduction half-equations:

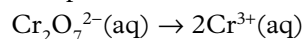


Step 3: Complete and balance each half-equation. Balance elements other than O and H first, then add  $\text{H}_2\text{O}$  and  $\text{H}^+$  to balance the O and H atoms. Finally, add electrons ( $e^-$ ) to balance charge.

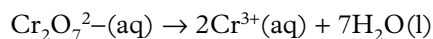
For the oxidation half-equation the Fe atoms are already balanced and no O or H atoms are present so we only need to add one electron to the RHS:



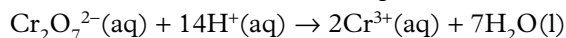
We take the same approach with the reduction half-equation. There are two Cr atoms on the LHS so we need to place a 2 in front of  $\text{Cr}^{3+}$  on the RHS:



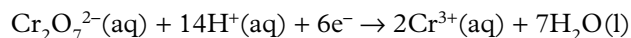
We note that there are seven O atoms on the LHS so we must place seven  $\text{H}_2\text{O}$  on the RHS:



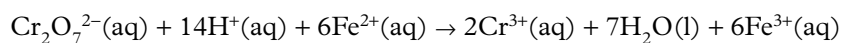
This results in 14 H atoms on the RHS so we place 14  $\text{H}^+$  ions on the LHS:



The total charge on the LHS is +12. The total charge on the RHS is +6. We therefore place six electrons on the LHS:



Step 4: We now add the two half-equations together to obtain the full redox equation. First, however, we note that there are uneven numbers of electrons appearing in both half-equations. We therefore need to multiply each half-equation by appropriate factors to ensure that there is an equal number of electrons lost in the oxidation half-equation as there is gained in the reduction half-equation. We do this by multiplying the oxidation half-equation by six; this gives six electrons on the RHS of this half-equation to match the six electrons on the LHS of the reduction half-equation. When we add these two half-equations together, the electrons will cancel:



This equation is now both mass-balanced and charge-balanced.



## Worked example 5.3.1

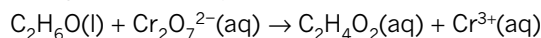
### BALANCING COMPLEX REDOX EQUATIONS (ACIDIC CONDITIONS)

|  |  |
|--|--|
| Balance the following equation using half-equations.<br>$\text{As}_4\text{O}_6(\text{s}) + \text{MnO}_4^-(\text{aq}) \rightarrow \text{AsO}_4^{3-}(\text{aq}) + \text{Mn}^{2+}(\text{aq})$   |  |
| <b>Thinking</b>  | <b>Working</b>   |
| Step 1. Calculate the oxidation numbers for each atom in the chemical equation (using the rules in Table 5.2.1 on page 134). Determine which atoms are undergoing oxidation and which are undergoing reduction.  | $\overset{+3}{\text{As}}\overset{-2}{\text{O}}_6(\text{s}) + \overset{+7}{\text{Mn}}\overset{-2}{\text{O}}_4^-(\text{aq}) \rightarrow \overset{+5}{\text{As}}\overset{-2}{\text{O}}_4^{3-}(\text{aq}) + \overset{+2}{\text{Mn}}^{2+}(\text{aq})$ <p>The oxidation number of As has increased from +3 to +5, so the arsenic in <math>\text{As}_4\text{O}_6</math> has been oxidised. The oxidation number of Mn in <math>\text{MnO}_4^-</math> has decreased from +7 to +2, so manganese has been reduced. The oxidation number for O has remained unchanged, so oxygen has not undergone oxidation or reduction.</p>   |
| Step 2. Split the reaction into two unbalanced half-equations, one containing the reactants and products for the oxidation process and one containing the reactants and products for the reduction process.  | $\text{As}_4\text{O}_6(\text{s}) \rightarrow \text{AsO}_4^{3-}(\text{aq}) \text{ (unbalanced oxidation half-equation)}$ $\text{MnO}_4^-(\text{aq}) \rightarrow \text{Mn}^{2+}(\text{aq}) \text{ (unbalanced reduction half-equation)}$   |
| Step 3. Formulate and balance each half-equation. They must be both mass-balanced and charge-balanced.<br>Balance elements other than O and H first, then add $\text{H}_2\text{O}$ and $\text{H}^+$ to balance the O and H atoms. Finally, add electrons ( $\text{e}^-$ ) to balance charge. | For the oxidation half-equation, four As atoms appear on the LHS so we place a '4' in front of $\text{AsO}_4^{3-}$ on the RHS:<br>$\text{As}_4\text{O}_6(\text{s}) \rightarrow 4\text{AsO}_4^{3-}(\text{aq})$ <p>This gives 16 O atoms on the RHS. We therefore add <math>10\text{H}_2\text{O}</math> to the LHS to balance O atoms (there are already six O atoms on the LHS):</p> $\text{As}_4\text{O}_6(\text{s}) + 10\text{H}_2\text{O}(\text{l}) \rightarrow 4\text{AsO}_4^{3-}(\text{aq})$ <p>This gives 20 H atoms on the LHS. We therefore add <math>20\text{H}^+</math> to the RHS:</p> $\text{As}_4\text{O}_6(\text{s}) + 10\text{H}_2\text{O}(\text{l}) \rightarrow 4\text{AsO}_4^{3-}(\text{aq}) + 20\text{H}^+(\text{aq})$ <p>The total charge on the LHS is zero. The total charge on the RHS = <math>4 \times -3 + 20 \times +1 = +8</math>. We therefore need to add <math>8\text{e}^-</math> to the RHS:</p> $\text{As}_4\text{O}_6(\text{s}) + 10\text{H}_2\text{O}(\text{l}) \rightarrow 4\text{AsO}_4^{3-}(\text{aq}) + 20\text{H}^+(\text{aq}) + 8\text{e}^-$ <p>Taking the same approach with the reduction half-equation, we note the Mn atoms are already balanced. We need to place <math>4\text{H}_2\text{O}</math> on the RHS to balance the O atoms. This gives eight H atoms on the RHS; we therefore place <math>8\text{H}^+</math> on the LHS. We balance the charge by adding <math>5\text{e}^-</math> to the LHS:</p> $\text{MnO}_4^- + 8\text{H}^+(\text{aq}) + 5\text{e}^- \rightarrow \text{Mn}^{2+}(\text{aq}) + 4\text{H}_2\text{O}(\text{l})$ |
| Step 4. Add the two half-equations together to obtain the final balanced redox equation.   | We note that there are uneven numbers of electrons appearing in both half-equations. We therefore need to multiply each half-equation by appropriate factors to ensure that there is an equal number of electrons lost in the oxidation half-equation as there is gained in the reduction half-equation. We do this by multiplying the oxidation half-equation by five and the reduction half-equation by eight; thus giving a total of 40 electrons in each half-equation. When we add these two half-equations together, the electrons will cancel:<br>$5\text{As}_4\text{O}_6(\text{s}) + 50\text{H}_2\text{O}(\text{l}) + 8\text{MnO}_4^-(\text{aq}) + 64\text{H}^+(\text{aq}) \rightarrow 20\text{AsO}_4^{3-}(\text{aq}) + 100\text{H}^+(\text{aq}) + 8\text{Mn}^{2+}(\text{aq}) + 32\text{H}_2\text{O}(\text{l})$ <p>This equation is now both mass-balanced and charge-balanced and simplifies to the following (after cancelling <math>\text{H}_2\text{O}</math> and <math>\text{H}^+</math> ions on both sides):</p> $5\text{As}_4\text{O}_6(\text{s}) + 18\text{H}_2\text{O}(\text{l}) + 8\text{MnO}_4^-(\text{aq}) \rightarrow 20\text{AsO}_4^{3-}(\text{aq}) + 36\text{H}^+(\text{aq}) + 8\text{Mn}^{2+}(\text{aq})$   |

### ► Try yourself 5.3.1

#### BALANCING COMPLEX REDOX EQUATIONS (ACIDIC CONDITIONS)

Construct the balanced redox equation for the reaction between ethanol and the dichromate ion to produce ethanoic acid and the chromium(III) ion, as represented by the following unbalanced equation:



## 5.3 Review

### SUMMARY

- The following steps must be taken to balance redox half-equations under acidic conditions.
  - 1 Balance all atoms except oxygen and hydrogen.
  - 2 Balance the oxygen atoms by adding  $\text{H}_2\text{O}$  molecules to one side of the half-equation.
  - 3 Balance the hydrogen atoms by adding  $\text{H}^+$  ions to one side of the half-equation.
  - 4 Balance the charge on both sides of the half-equation by adding electrons ( $e^-$ ) to the side with the greater positive charge.
  - 5 Indicate whether each substance exists as a dissolved solute or as a solid, liquid or gas by inserting the appropriate label.
- To construct an overall equation, add the oxidation half-equation and the reduction half-equation, making sure that the number of electrons used in reduction equals the number of electrons released during oxidation.
- When combining oxidation and reduction half-equations under acidic conditions, any  $\text{H}^+(\text{aq})$  and  $\text{H}_2\text{O}(\text{l})$  that appear on both sides of the arrow should be cancelled down.

### KEY QUESTIONS

#### Retrieval

- 1 Select the correct word to complete the following sentences.
  - a Electrons appear on the **left-hand/right-hand** side of a half-equation for oxidation half-equations.
  - b Electrons appear on the **left-hand/right-hand** side of a half-equation for reduction half-equations.
- 2 List the steps for balancing redox half-equations in acidic conditions.

#### Comprehension

- 3 Determine half-equations for the:
  - a reduction of  $\text{MnO}_2$  to  $\text{Mn}^{2+}$
  - b reduction of  $\text{MnO}_4^-$  to  $\text{MnO}_2$
  - c reduction of  $\text{SO}_4^{2-}$  to  $\text{H}_2\text{S}$
  - d oxidation of  $\text{SO}_2$  to  $\text{SO}_4^{2-}$
  - e oxidation of  $\text{H}_2\text{S}$  to  $\text{S}$
  - f oxidation of  $\text{SO}_3^{2-}$  to  $\text{SO}_4^{2-}$ .
- 4 When zinc powder is sprinkled into an acidified solution of potassium dichromate ( $\text{K}_2\text{Cr}_2\text{O}_7$ ), a reaction occurs that produces zinc ions and chromium(III) ions in solution. The potassium ions are spectator ions and the net reaction is between  $\text{Zn}(\text{s})$  and  $\text{Cr}_2\text{O}_7^{2-}(\text{aq})$  ions.
  - a Determine the oxidation half-equation for the reaction.
  - b Determine the reduction half-equation for the reaction.
  - c Use your answers to parts **a** and **b** to construct a balanced equation for the overall reaction.

- 5 Construct the half-equations and the balanced overall equation for the reaction in which:
  - a a solution containing iron(II) ions is oxidised by an acidified solution containing dichromate ions ( $\text{Cr}_2\text{O}_7^{2-}$ ). The products include iron(III) and chromium(III) ions
  - b a solution containing sulfite ions ( $\text{SO}_3^{2-}$ ) reacts with an acidified solution of permanganate ions ( $\text{MnO}_4^-$ ) to produce a colourless solution containing sulfate ions and manganese(II) ions
  - c manganese dioxide ( $\text{MnO}_2$ ) reacts with concentrated hydrochloric acid to form chlorine gas and a solution containing manganese(II) ions.

#### Analysis

- 6 Classify each of the following as 'redox' or 'not redox'.
  - a  $\text{Zn}(\text{s}) + \text{H}_2\text{SO}_4(\text{aq}) \rightarrow \text{ZnSO}_4(\text{aq}) + \text{H}_2(\text{g})$
  - b  $\text{LiCl}(\text{aq}) + \text{AgNO}_3(\text{aq}) \rightarrow \text{LiNO}_3(\text{aq}) + \text{AgCl}(\text{s})$
  - c  $\text{AgNO}_3(\text{aq}) + \text{HCl}(\text{aq}) \rightarrow \text{AgCl}(\text{s}) + \text{HNO}_3(\text{aq})$
  - d  $\text{C}(\text{s}) + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})$
  - e  $\text{H}_2\text{CO}_3(\text{aq}) + \text{Ca}(\text{NO}_3)_2(\text{aq}) \rightarrow 2\text{HNO}_3(\text{aq}) + \text{CaCO}_3(\text{s})$
- 7 As a result of a traffic accident, residents in a Gold Coast suburb had to be evacuated when toxic fumes leaked from a container of sodium dithionite ( $\text{Na}_2\text{S}_2\text{O}_4$ ). The dithionite ion reacts with water according to the equation:
$$2\text{S}_2\text{O}_4^{2-}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{S}_2\text{O}_3^{2-}(\text{aq}) + 2\text{HSO}_3^-(\text{aq})$$
  - a State the oxidation number of the sulfur in the following ions.
    - i  $\text{S}_2\text{O}_4^{2-}$
    - ii  $\text{S}_2\text{O}_3^{2-}$
    - iii  $\text{HSO}_3^-$
  - b Determine half-equations for the oxidation and reduction reactions that occur when sodium dithionite is mixed with water.



## Simple displacement reactions



### Research and planning

#### Aim

- To perform a series of single displacement reactions in aqueous solution.
- To determine a reactivity series based on the results of single displacement reactions.

#### Rationale (scientific background to the experiment)

By definition, reduction is a gain of electrons and oxidation is a loss of electrons. In single displacement reactions in aqueous solutions, the metal loses its electrons to the metal ion in solution. This is a redox reaction. The metal losing its electrons is the reductant and the metal gaining electrons is the oxidant.

Single displacement reactions only occur if the metal is more reactive than the metal ions in solution and as such will give away its electrons. A reactivity series can be developed based on this, with the more reactive metals, those more easily oxidised, sitting higher in the series than those less easily oxidised.

#### Timing

50 minutes

#### Materials

- 5 × small clean strips or pieces of each of the following metals: Mg, Zn, Ag, Cu
- 5 × iron nails (not galvanised)
- 5 × test tubes and test-tube rack
- 25 mL × 0.1 mol L<sup>-1</sup> solutions of the following cations: Mg<sup>2+</sup>, Zn<sup>2+</sup>, Ag<sup>+</sup>, Cu<sup>2+</sup> and Fe<sup>2+</sup> (The anions in these salts could be any of nitrates, sulfates or chlorides.)
- safety glasses

#### Safety

- Wear safety glasses and a laboratory coat.
- Take care to rinse off any aqueous solution that may spill on your body.

#### Method

##### Risk assessment

Assessment of risks include chemical hazards and physical hazards. Before you commence this practical activity, you must conduct a risk assessment. Complete the template in your skills and assessment book or download it from your eBook.

- Examine the following table, which shows the possible combinations of metals and metal ion salt aqueous solutions.  
Set up the five test tubes in the test-tube rack and add 5 mL of the first metal ion salt solution from the table to each.
- Place a piece of each of the different metals in a different test tube and observe.
- Record your findings in the results table.
- Discard contents of all test tubes and set up again as in step 1, using the second metal ion salt aqueous solution from the table.
- Repeat steps 2 and 3 using fresh metal samples.
- Continue until all five solutions have been used.

#### Variables

- Independent: the combination of metal and metal ion salt aqueous solution used in the reaction.
- Dependent: if a reaction occurs and the rate of the redox reaction.
- Controlled: the amount of metal used, the volume and concentration of the metal ion salt aqueous solution used.

### Analysing

#### Raw data

- Create a table to illustrate whether reactions occurred between metal and metal ions in solution. Use your table to record if there is a reaction (✓) or no reaction (✗).

| Metal | Aqueous solution |                  |                  |                 |                  |
|-------|------------------|------------------|------------------|-----------------|------------------|
|       | Mg <sup>2+</sup> | Zn <sup>2+</sup> | Fe <sup>2+</sup> | Ag <sup>+</sup> | Cu <sup>2+</sup> |
| Mg    |                  |                  |                  |                 |                  |
| Zn    |                  |                  |                  |                 |                  |
| Fe    |                  |                  |                  |                 |                  |
| Ag    |                  |                  |                  |                 |                  |
| Cu    |                  |                  |                  |                 |                  |

#### Processed data

- Using your results from question 1, deduce which was the:
  - most reactive metal
  - least reactive metal.

- 3 Determine half-equations for each reaction that occurred.

| Reaction | Reduction half-equation | Oxidation half-equation |
|----------|-------------------------|-------------------------|
|          |                         |                         |
|          |                         |                         |
|          |                         |                         |
|          |                         |                         |
|          |                         |                         |
|          |                         |                         |
|          |                         |                         |
|          |                         |                         |
|          |                         |                         |
|          |                         |                         |

**Reflect and check that your data analysis demonstrates these characteristics**

- Effective investigation of phenomena is demonstrated by the collection of sufficient and relevant raw data.
- Accurate application of algorithms, visual and graphical representations of data is demonstrated by appropriate processing and presentation of data to aid the analysis and interpretation of data.

**Analysis**

- 4 Analyse your results table and create a reactivity series listing the reduction half-equations from the strongest oxidant at the top to the weakest oxidant at the bottom.
- 5 Compare and contrast the reactivity series you have created with Figure 5.1.8 on page 124. Identify why there might be differences between your table and the one in the textbook.

**Reflect and check that your analysis demonstrates these characteristics**

- Systematic and effective analysis of evidence is demonstrated by a thorough and appropriate error analysis.
- Systematic and effective analysis of evidence is demonstrated by a thorough identification of relevant trends, patterns and relationships.
- Insightful and valid interpretation of evidence is demonstrated by drawing a valid and defensible conclusion based on the analysis.

**Interpreting and communicating**
**Conclusion**

- 1
  - a From the analysis of your results, determine what conclusions can be inferred.
  - b Explain the evidence that leads you to these conclusions.

**Evaluation**

- 2 Assess your analysis and conclusions. Identify whether the experiment provided an effective and efficient method of determining the reactivity series of metals. Explain your evaluation.

**Improvements**

- 3 Critique the experiment. If you were to repeat the experiment, identify the steps that you would do differently. Discuss the following in your answer.
  - a Analyse how you would change the methodology to help improve the accuracy of the results.
  - b Evaluate how you performed the tasks and the skills that you need to improve on in your technique.
  - c Explain how the collection of data could be improved or uncertainty reduced.

**Reflect and check that your evaluation demonstrates these characteristics**

- Critical evaluation of processes is demonstrated by a discussion of the reliability and validity of the experimental process supported by evidence such as the quality of the data (as quantified in the error analysis).
- Critical evaluation of the conclusion is demonstrated by a discussion of the veracity of the conclusions with respect to the error analysis and limitations or sufficiency of the data.
- Insightful evaluation of processes and conclusions is demonstrated by a suggestion of improvements or extensions to the experiment which are logically derived from the analysis of the evidence.

# Chapter review

# 05

## KEY TERMS

alloy  
anode  
cathode  
cathodic protection  
conjugate redox pair  
direct corrosion  
displace  
dry corrosion

electroplating  
half-equation  
main group metal  
metal displacement  
reaction  
oxidant  
oxidation  
oxidation number

oxidation state  
oxidised  
oxidising agent  
reactivity series of metals  
redox reaction  
reduced  
reducing agent  
reductant

reduction  
sacrificial anode  
sacrificial protection  
spontaneous redox reaction  
transition element  
wet corrosion

## KEY QUESTIONS

### Retrieval

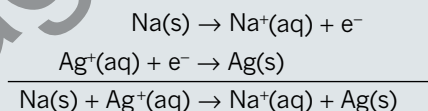
- List the overall steps for balancing full redox equations in acidic conditions.
- State why oxidation and reduction must occur simultaneously in redox reactions.
- State what process the metal atoms have undergone when pure metals are extracted from their oxide ores.
- Determine whether each of the following statements is true or false.
  - Group 1 and 2 metal ions, such as  $\text{Na}^+$ , are reducing agents because they tend to lose electrons.
  - Group 17 molecules, such as  $\text{I}_2$ , can be oxidising agents or reducing agents.
  - Non-metal ions, such as  $\text{Cl}^-$ , can be reducing agents because they can lose electrons.
  - Metals, such as  $\text{Cu}$ , can be oxidising agents because they can gain electrons.
- Deduce the correct missing terms by completing the following sentences that describe oxidation and reduction.

Oxidation and reduction occur together. Oxidation occurs when an atom \_\_\_\_\_ electrons to form a \_\_\_\_\_ ion, such as when a calcium atom, with an electronic configuration of 2, 8, 8, 2, \_\_\_\_\_ electrons to form a  $\text{Ca}^{2+}$  ion. Reduction occurs when an atom \_\_\_\_\_ electrons to form a \_\_\_\_\_ ion or when a cation \_\_\_\_\_ electrons to become a neutral atom. An example is when a bromine atom, with \_\_\_\_\_ electrons in its valence shell, \_\_\_\_\_ an electron to form a \_\_\_\_\_ ion.

- List the following in terms of increasing reducing strength.  
 $\text{K}$ ,  $\text{Cu}$ ,  $\text{Sn}$ ,  $\text{Mg}$ ,  $\text{Zn}$ .

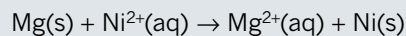
### Comprehension

- Consider the following half-equations and the overall equation for the reaction between sodium metal and a solution of silver ions.



Determine which one of the following sets of statements correctly describes this redox reaction.

- $\text{Na(s)}$  is the reducing agent,  $\text{Ag}^+(\text{aq})$  is the oxidising agent, sodium metal is oxidised.
  - $\text{Na(s)}$  is the oxidising agent,  $\text{Ag}^+(\text{aq})$  is the reducing agent, sodium metal is reduced.
  - $\text{Na(s)}$  is the reducing agent,  $\text{Ag}^+(\text{aq})$  is the oxidising agent, sodium metal is reduced.
  - $\text{Na}^+(\text{aq})$  is the oxidising agent,  $\text{Ag(s)}$  is the reducing agent, sodium metal is oxidised.
- Magnesium reacts with nickel(II) ions according to the following equation:



Determine which one of the following is the correct set of conjugate redox pairs for this reaction.

- $\text{Mg}^{2+}(\text{aq})/\text{Mg(s)}$  and  $\text{Ni}^{2+}(\text{aq})/\text{Ni(s)}$
  - $\text{Ni(s)}/\text{Mg}^{2+}(\text{aq})$  and  $\text{Ni}^{2+}(\text{aq})/\text{Mg(s)}$
  - $\text{Mg(s)}/\text{Ni(s)}$  and  $\text{Ni}^{2+}(\text{aq})/\text{Mg}^{2+}(\text{aq})$
  - $\text{Mg(s)}/\text{Ni}^{2+}(\text{aq})$  and  $\text{Ni(s)}/\text{Mg}^{2+}(\text{aq})$
- Determine which one of the following alternatives describes what happens when sodium and oxygen react.
    - Each sodium atom gains one electron.
    - Each sodium atom loses one electron.
    - Each oxygen atom gains one electron.
    - Each oxygen atom loses one electron.

- 10** Determine which one of the following redox equations has not been balanced correctly.
- A**  $\text{Zn}^{2+}(\text{aq}) + \text{Mg}(\text{s}) \rightarrow \text{Zn}(\text{s}) + \text{Mg}^{2+}(\text{aq})$   
**B**  $\text{Cu}^{2+}(\text{aq}) + \text{Zn}(\text{s}) \rightarrow \text{Cu}(\text{s}) + \text{Zn}^{2+}(\text{aq})$   
**C**  $\text{Fe}^{2+}(\text{aq}) + \text{Zn}(\text{s}) \rightarrow \text{Fe}(\text{s}) + \text{Zn}^{2+}(\text{aq})$   
**D**  $\text{Ag}^{+}(\text{aq}) + \text{Cu}(\text{s}) \rightarrow \text{Ag}(\text{s}) + \text{Cu}^{2+}(\text{aq})$
- 11** Determine which one of the following factors does not increase the rate of corrosion of a metal object.
- A** The presence of water with dissolved oxygen.  
**B** The presence of acidic pollutants dissolved in water.  
**C** The presence of impurities, such as salt, dissolved in water.  
**D** The presence of a coating of paint over the surface of the metal object.
- 12** Deep-sea divers sometimes report that the metal on vessels they find on the seabed does not appear to have corroded. Determine which one of the following might contribute to the lack of corrosion.
- A** Deep-sea creatures eat iron oxide.  
**B** A lack of light prevents corrosion from occurring.  
**C** There is little oxygen dissolved in the water near the seabed.  
**D** The concentration of dissolved salt in the sea decreases with increasing depth.
- 13** Explain the term 'electrochemical protection' of iron.
- 14** Calculate the oxidation number of sulfur in each of the following compounds.
- a**  $\text{SO}_2$   
**b**  $\text{H}_2\text{S}$   
**c**  $\text{H}_2\text{SO}_4$   
**d**  $\text{SO}_3$   
**e**  $\text{Na}_2\text{SO}_3$   
**f**  $\text{Na}_2\text{S}_2\text{O}_3$
- 15** Show your understanding of oxidation numbers and elements by completing the following table.

| Compound                | Element | Oxidation number |
|-------------------------|---------|------------------|
| $\text{CaCO}_3$         | Ca      |                  |
| $\text{HNO}_3$          | O       |                  |
| $\text{H}_2\text{O}_2$  |         | -1               |
| $\text{HCO}_3^-$        |         | +4               |
| $\text{HNO}_3$          | N       |                  |
| $\text{KMnO}_4$         |         | +7               |
| $\text{H}_2\text{S}$    | S       |                  |
| $\text{Cr}_2\text{O}_3$ | Cr      |                  |
| $\text{N}_2\text{O}_4$  | N       |                  |

- 16** Copper bowls and trays can be decorated by etching patterns on them using concentrated nitric acid. The overall reaction is:
- $$\text{Cu}(\text{s}) + 4\text{HNO}_3(\text{aq}) \rightarrow \text{Cu}(\text{NO}_3)_2(\text{aq}) + 2\text{NO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l})$$
- a** Determine what the oxidation number of copper is:
- i** before the reaction  
**ii** after the reaction.
- b** Determine the oxidation number of nitrogen:
- i** before the reaction  
**ii** after the reaction.
- c** Name the oxidising agent and reducing agent in this process.
- 17** Show your understanding of conjugate pairs by completing the following table, giving the conjugate redox pairs for each of the reactions.

| Equation   | Conjugate redox pair (oxidation) | Conjugate redox pair (reduction) |
|--|----------------------------------|----------------------------------|
| $\text{Fe}(\text{s}) + \text{I}_2(\text{aq}) \rightarrow \text{FeI}_2(\text{aq})$  |                                  |                                  |
| $\text{Mg}(\text{s}) + \text{FeCl}_2(\text{aq}) \rightarrow \text{MgCl}_2(\text{aq}) + \text{Fe}(\text{s})$  |                                  |                                  |
| $10\text{Br}^-(\text{aq}) + 2\text{MnO}_4^-(\text{aq}) + 16\text{H}^+(\text{aq}) \rightarrow 2\text{Mn}^{2+}(\text{aq}) + 8\text{H}_2\text{O}(\text{l}) + 5\text{Br}_2(\text{aq})$ |                                  |                                  |
| $\text{Cu}(\text{s}) + 2\text{NO}_3^-(\text{aq}) + 4\text{H}^+(\text{aq}) \rightarrow \text{Cu}^{2+}(\text{aq}) + 2\text{NO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l})$          |                                  |                                  |



- 18 Complete the summary below as you balance the half-equation for the reduction of  $\text{NO}_3^-$  to  $\text{NO}_2$  in acidic solution:  
 $\text{NO}_3^-(\text{aq}) \rightarrow \text{NO}_2(\text{g})$

| Step | Task   | How it's done   | Half-equation  |
|------|--|---|--|
| 1    | Balance nitrogens.                                 |   | $\text{NO}_3^-(\text{aq}) \rightarrow \text{NO}_2(\text{g})$ |
| 2    | Balance oxygens by adding _____.                   | Add _____ $\text{H}_2\text{O}$ molecule(s) to right-hand side of the equation.  |  |
| 3    | Balance hydrogens by adding _____.                 | Add _____ $\text{H}^+$ ion(s) to _____ of the equation.   |  |
| 4    | Balance charge by adding _____.                    | Charge on left-hand side = _____<br>Charge on right-hand side = _____<br>Add _____ $\text{e}^-$ to the _____ of the equation. |  |
| 5    | Add state symbols to give the final half-equation. | Give the appropriate states for each reactant and product in the equation.  |  |

- 19 During each of the following analyses, redox reactions occurred. Construct half-equations for the oxidation and reduction reactions. Use these half-equations to construct an overall equation for each reaction.

- a Zinc was reduced by reacting it with a solution of  $\text{Pb}^{2+}$  ions. Lead metal was precipitated and  $\text{Zn}^{2+}$  ions were formed.
- b The amount of  $\text{Fe}^{2+}$  ions in iron tablets was determined by oxidising them to  $\text{Fe}^{3+}$  ions using an acidified solution of  $\text{MnO}_4^-$  ions. The  $\text{MnO}_4^-$  ions were reduced to  $\text{Mn}^{2+}$  ions during the reaction.
- c Sulfur dioxide ( $\text{SO}_2$ ), a preservative in dried fruit, was determined by oxidation to  $\text{SO}_4^{2-}$  using a solution of  $\text{I}_2$ . Iodide ( $\text{I}^-$ ) ions were produced.
- d An acidified solution of bleach, which contains  $\text{OCl}^-$  ions, was titrated against a solution of  $\text{I}^-$  ions. The reaction products included  $\text{Cl}^-$  and  $\text{I}_2$ .

- 20 In dry cells commonly used in torches, an electric current is produced from the reaction of zinc metal with solid manganese oxide ( $\text{MnO}_2$ ). During this reaction,  $\text{Zn}^{2+}$  ions and solid  $\text{Mn}_2\text{O}_3$  are formed. Show half-equations, and hence an overall equation, for the reaction.

- 21 The following equations are not balanced.
- Identify the species that has been reduced and the species that has been oxidised.
  - Show balanced half-equations for the oxidation and reduction reactions.
  - Combine the half-equations to show a balanced overall equation.
- a  $\text{Ce}^{4+}(\text{aq}) + \text{H}_2\text{S}(\text{g}) \rightarrow \text{Ce}^{3+}(\text{aq}) + \text{S}(\text{s}) + \text{H}^+(\text{aq})$
- b  $\text{NO}_3^-(\text{aq}) + \text{H}^+(\text{aq}) + \text{Cu}(\text{s}) \rightarrow \text{NO}(\text{g}) + \text{H}_2\text{O}(\text{l}) + \text{Cu}^{2+}(\text{aq})$
- c  $\text{H}_2\text{O}_2(\text{aq}) + \text{Br}^-(\text{aq}) + \text{H}^+(\text{aq}) \rightarrow \text{Br}_2(\text{l}) + \text{H}_2\text{O}(\text{l})$
- d  $\text{MnO}_2(\text{s}) + \text{H}^+(\text{aq}) + \text{S}(\text{s}) \rightarrow \text{Mn}^{2+}(\text{aq}) + \text{H}_2\text{O}(\text{l}) + \text{SO}_2(\text{g})$

### Analysis

- 22 Sort the following substances in order of increasing oxidation states of nitrogen.  
 $\text{NO}$ ,  $\text{K}_3\text{N}$ ,  $\text{N}_2\text{O}_4$ ,  $\text{N}_2\text{O}$ ,  $\text{Ca}(\text{NO}_3)_2$ ,  $\text{N}_2\text{O}_3$ ,  $\text{N}_2$
- 23 Consider the following products that are made during the wet corrosion of iron. Put them in the correct order in which they are made.  
 $\text{Fe}(\text{OH})_3(\text{s})$ ,  $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ ,  $\text{Fe}(\text{OH})_2(\text{s})$ ,  $\text{Fe}^{2+}(\text{aq})$ ,  $\text{OH}^-(\text{aq})$
- 24 Iron reacts with hydrochloric acid according to the ionic equation:
- $$\text{Fe}(\text{s}) + 2\text{H}^+(\text{aq}) \rightarrow \text{Fe}^{2+}(\text{aq}) + \text{H}_2(\text{g})$$
- Determine what has been oxidised in this reaction.
  - Determine what the product of oxidation is.
  - Construct the half-equation for the oxidation reaction.
  - Identify the oxidising agent.
  - Determine what has been reduced in this reaction and the product of reduction.
  - Construct the half-equation for the reduction reaction.
  - Identify the reducing agent.
- 25 Calcium metal that is exposed to the air forms an oxide coating.
- Determine the formula of calcium oxide.
  - Deduce what has been oxidised in this reaction.
  - Show a half-equation for the oxidation reaction.
  - Determine what has been reduced in this reaction.
  - Show a balanced half-equation for the reduction reaction.
  - Show an overall equation for this redox reaction.
  - Deduce the correct missing terms by completing the following sentences.

Calcium has been \_\_\_\_\_ by \_\_\_\_\_ to calcium ions. The \_\_\_\_\_ has gained electrons from the \_\_\_\_\_. The oxygen has been \_\_\_\_\_ by \_\_\_\_\_ to oxide ions. The \_\_\_\_\_ has lost electrons to the \_\_\_\_\_.

- 26** In the following redox reactions, determine which species have been oxidised and which have been reduced.
- $\text{Cu}^{2+}(\text{aq}) + \text{Mg}(\text{s}) \rightarrow \text{Cu}(\text{s}) + \text{Mg}^{2+}(\text{aq})$
  - $\text{Zn}(\text{s}) + 2\text{Ag}^{+}(\text{aq}) \rightarrow \text{Zn}^{2+}(\text{aq}) + 2\text{Ag}(\text{s})$
  - $\text{PbO}(\text{s}) + \text{CO}(\text{g}) \rightarrow \text{Pb}(\text{s}) + \text{CO}_2(\text{g})$
  - $\text{Ca}(\text{s}) + 2\text{HCl}(\text{aq}) \rightarrow \text{CaCl}_2(\text{aq}) + \text{H}_2(\text{g})$
  - $\text{Pb}^{2+}(\text{aq}) + \text{Fe}(\text{s}) \rightarrow \text{Pb}(\text{s}) + \text{Fe}^{2+}(\text{aq})$
- 27** When zinc reacts with a solution of hydrochloric acid, hydrogen gas is produced.
- Determine what has been oxidised in this reaction.
  - Construct the half-equation for the oxidation reaction.
  - Determine what has been reduced in this reaction.
  - Construct the half-equation for the reduction reaction.
  - Identify the oxidising agent.
  - Identify the reducing agent.
  - Construct the overall equation for this redox reaction.
- 28** An unknown metal is placed in solutions of aluminium nitrate and iron(II) sulfate. After a period of time, the metal is found to have reacted with the iron(II) sulfate solution, but not the aluminium nitrate solution. Determine a possible identity of the unknown metal.
- 29** Iron nails are placed into solutions of  $\text{CuSO}_4$ ,  $\text{MgCl}_2$ ,  $\text{Pb}(\text{NO}_3)_2$  and  $\text{ZnCl}_2$ . Predict in which solutions you would expect a coating of another metal to appear on the nail. Explain your answer.
- 30** Determine why it is usually not necessary to protect structures made of copper from corrosion.
- 31** The iron in galvanised iron nails is protected from corrosion by a coating of zinc. Explain why a coating of tin instead of zinc would not be appropriate protection for iron nails.
- 32** Explain why steel garden furniture rusts more readily in coastal areas than it does inland.
- 33** Determine whether elements from the following groups would be more likely to be oxidised or reduced when they take part in chemical reactions with the other group.
- Group A: sodium, calcium and magnesium  
Group B: sulfur, oxygen and chlorine
- 34** Solid ammonium dichromate decomposes to form chromium(III) oxide, nitrogen gas and steam.
- Calculate the oxidation numbers of chromium and nitrogen in the reactant ammonium dichromate ( $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ ) and the products  $\text{Cr}_2\text{O}_3$  and  $\text{N}_2$ . Identify which reactants have been reduced and oxidised.
  - Complete and balance the following half-equations.
    - $\text{NH}_4^{+}(\text{s}) \rightarrow \text{N}_2(\text{g})$
    - $\text{Cr}_2\text{O}_7^{2-}(\text{s}) \rightarrow \text{Cr}_2\text{O}_3(\text{s})$
  - Identify each of the half-equations in part **b** as either reduction or oxidation processes and explain your answer in terms of oxidation numbers.
  - Construct the balanced overall equation for the reaction that occurs.
  - Identify the conjugate redox pairs for the reaction.
- Knowledge utilisation**
- 35** Create a concept map that shows the links between the following terms: redox reactions, oxidising agent, reducing agent, electrons, oxidation, reduction.
- 36** Predict which of the following food cans best protect its food contents. Support your decision by referring to the relative ease of oxidation.
- an intact steel food can
  - a dented steel food can
  - an intact steel food can lined with zinc
  - a dented steel food can lined with zinc
  - an intact steel food can lined with tin
  - a dented steel food can lined with tin